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NEW MEMBRANES FOR REVERSE OSMOSIS TREATMENT OF METAL FINISHING EFFLUENTS

Lee T. Rozelle, et al

North Star Research Institute

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Simulated alkaline copper and zinc cyanide plating rinses at pH's of 11.8 and 12.9 were treated by NS-1 membranes during 500- and 340-hour tests without deterioration of reverse osmosis properties. Water fluxes above 10 gallons per square foot (of membrane) per day (gfd) were observed with cyanide rejections between 95 and 99 percent. The NS-1 membrane also treated simulated copper sulfate rinse waters effectively at pH 0.5 during 550-hour tests without deterioration of reverse osmosis properties (fluxes above 10 gfd with 99.8 percent rejection of copper). The NS-1 membrane is the only known membrane that can perform well using both acidic and alkaline feed solutions.

Preliminary engineering considerations indicated the feasibility of applying the NS-1 membrane to reverse osmosis treatment and recycle of nickel and zinc cyanide electroplating rinse waters.

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NEW MEMBRANES FOR REVERSE OSMOSIS TREATMENT OF METAL FINISHING EFFLUENTS

by

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Program Element 1BB036

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ABSTRACT

An important new membrane has been developed for the reverse osmosis treatment of both highly alkaline and acidic (non-oxidizing) metal finishing rinse waters. This membrane, designated NS-1, and originally developed for seawater desalination, consists of the following: a microporous support film (polysulfone) coated with polyethylenimine which is cross-linked with tolylene 2,4-diisocyanate.

Simulated alkaline copper and zinc cyanide plating rinses at pH's of 11.8 and 12.9 were treated by NS-1 membranes during 500- and 340-hour tests without deterioration of reverse osmosis properties. Water fluxes above 10 gallons per square foot (of membrane) per day (gfd) were observed with cyanide rejections between 95 and 99 percent. The NS-1 membrane also treated simulated copper sulfate rinse waters effectively at pH 0.5 during 550-hour tests without deterioration of reverse osmosis properties (fluxes above 10 gfd with 99.8 percent rejection of copper). The NS-1 membrane is the *only* known membrane that can perform well using both acidic and alkaline feed solutions.

Preliminary engineering considerations indicated the feasibility of applying the NS-1 membrane to reverse osmosis treatment and recycle of nickel and zinc cyanide electroplating rinse waters.

Tubular development studies were performed on three ultrathin membranes [cellulose acetate (E 398-10), β-glucan acetate dimethylaminoethyl ether (β-GADE), and cellulose acetate O-propyl sulfonic acid (CAOPSA)] which showed promise as flat sheets during Phase I for treating slightly acidic metal finishing wastewaters. Cellulose acetate (E 398-10) and CAOPSA were successfully cast in 1/2-inch-ID tubes but β-GADE membranes were not. The spiral wrap configuration may be most effective for the β-GADE membranes.

This report was submitted in fulfillment of Project 12010 DRH under the partial sponsorship of the U. S. Environmental Protection Agency.

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SECTION I

CONCLUSIONS

This study has led to the following conclusions regarding the treatment of metal finishing wastewaters by reverse osmosis:

1. An important new membrane that is a major breakthrough in the reverse osmosis treatment of both highly alkaline and acidic (non-oxidizing) rinse waters has been developed. This membrane, derived from a non-polysaccharide polymer, is designated NS-1 and was originally developed by North Star under Office of Saline Water funding for seawater desalination. This membrane consists of the following: polyethylenimine (PEI)-coated microporous support (polysulfone) reacted with m-tolylene 2,4-diisocyanate (TDI). The NS-1 membrane has shown considerable promise as an effective membrane for the reverse osmosis treatment of:

   a. Cyanide rinse waters. Simulated alkaline copper and zinc cyanide plating bath rinses at pH's of 11.8 and 12.9 were effectively treated by NS-1 membranes for periods of 500 and 340 hours under pressures of 600 psi without membrane deterioration. At the conclusion of the copper and zinc plating bath tests the average cyanide rejections were 98.5 and 95.5 percent, respectively. The membrane also rejected 99.8 and 99.9 percent of the copper and zinc ions present in the feed, with an average product flux of 11 gallons per square foot (of membrane) per day (gfd).

   b. Acidic non-oxidizing metal finishing wastes. The NS-1 membrane was found to be effective for the treatment of acidic non-oxidizing metal finishing wastes containing divalent ions. During long-term tests on copper sulfate simulated rinse waters at a pH of 0.5 the NS-1 membrane exhibited: no membrane degradation during 550-hour tests, an average water flux of 9.1 gfd after 550 hours of testing, and high rejection of copper ions (99.8 percent).

2. The very promising reverse osmosis properties observed for the flat-cast ultrathin membranes during Phase I could not be achieved in the tubular configuration

within the scope of this program. The tubular development studies were performed on three membranes which showed promise in Phase I for treating acidic wastewaters. The results of these studies are as follows:

a. Cellulose acetate (E398-10) ultrathin membranes may be successfully cast in 1/2-inch-ID tubes, but it was decided that a membrane of this polymer did not represent a major improvement over commercially available reverse osmosis membranes for the treatment of metal finishing waste.

b. Ultrathin β-glucan acetate dimethylaminoethyl ether (β-GADE) membranes could not be cast in 1/2-inch-ID tubes.

c. Cellulose acetate O-propyl sulfonic acid (CAOPSA) ultrathin membranes were successfully cast in 1/2-inch-ID tubes by compensating for the inelasticity present in the polymer. Adequate flux and salt rejection (23 gfd and 92 percent) were obtained from these tubes.

Further tubular casting development would be expected to result in effective membranes of β-GADE and CAOPSA. However, the high flux and rejection properties of these ultrathin membranes, observed in flat sheets, could be realized in the spiral wrap configuration for reverse osmosis treatment of metal finishing wastewaters.

3. Preliminary design concepts were developed on the application of reverse osmosis treatment of zinc cyanide and Watts nickel plating rinse waters using the NS-1 membrane. The product water (water which has permeated through the reverse osmosis membrane) was recycled back into the rinse bath and the concentrate recycled back to the plating bath. An equation was derived that accurately estimates the concentration values for the product water and concentrate by knowing (1) the fraction of dissolved material rejected by the membrane and (2) the fractional reduction in feed volume exhibited by the reverse osmosis module. The calculation shows that a 99+ percent recovery of metal salts and water is feasible when a reverse osmosis system, utilizing the NS-1 membrane, is applied to the two metal plating operations.

SECTION II

RECOMMENDATIONS

The overall purpose of this research program was to develop and evaluate new membranes for improved metal finishing waste treatment by reverse osmosis. The major tasks of this second phase were (1) the development of those membranes found most promising in Phase I into tubular configurations and (2) the evaluation and development of new second generation reverse osmosis membranes.

An important new membrane, designated NS-1 and developed by North Star was observed to treat both highly alkaline and acidic (non-oxidizing) rinse waters effectively using the reverse osmosis process. This is the only known membrane with both acid and base stability and it constitutes a major breakthrough in reverse osmosis treatment of waste streams. It is, thus, strongly recommended that the application of the NS-1 membrane to reverse osmosis treatment of metal finishing waste effluents be continued to the field-demonstration phase.

In order to arrive at the field-demonstration phase, the following three major tasks are recommended:

- Determine a set of casting procedures for fabricating tubular membranes with consistently optimum performance for water-flux and metal ion rejection on metal finishing waste streams (*e.g.*, 20 gfd flux combined with over 95 percent cyanide rejection for zinc cyanide rinse waters). There is a specific need to develop casting processes for tubular NS-1 membranes in order to achieve consistent membrane performance and quality for waste treatment on a commercial scale. This task should thus include (1) optimization of the polysulfone casting procedure (*e.g.*, determine and fabricate its optimum thickness); (2) establishment of optimum PEI-TDI coating sequences; (3) development of optimum reaction variables for the formulation of NS-1 membranes such as coating concentration and cure temperatures.

- Long-term testing on simulated metal finishing rinse waters in order to establish performance capabilities and reliability of the NS-1 membrane in prolonged operation under field conditions. Tests of at least 1000 hours should be performed on alkaline and acid metal finishing rinse waters using the optimum NS-1 membrane.

- Determination of the rejections for typical plating bath additives, including various inorganic and organic compounds that are currently used. This task will provide insight for the total design and performance of the reverse osmosis system in a metal finishing waste solution.

- Engineering design studies and economic analysis of both NS-1 membrane production and utilization in a reverse osmosis system must be carried out to prepare for the large-scale field-demonstration.

SECTION III

INTRODUCTION

North Star Research Institute has completed the second phase of research on the program "The Use of Reverse Osmosis for Treating Metal Finishing Effluents". The Minnesota Pollution Control Agency, as grantee from the U. S. Environmental Protection Agency, together with five private organizations, sponsored the work as EPA Program No. 12010 DBH.

The program was designed to serve the needs of the metal finishing industry through improved pollution control and efficient conservation of valuable materials. During Phase I[1] of this program the treatment of metal finishing wastewaters by reverse osmosis was shown to be feasible. A number of membranes, both commercially available and improved new types, were demonstrated to be capable of treating various metal finishing effluents. The second phase of this program, described in this report, consisted of (1) fabrication and testing of membranes, found most promising in Phase I, in tubular configurations and (2) developing new second generation membranes for improved metal finishing waste treatment by reverse osmosis.

Background

General

The metal finishing industry has an ever-growing problem in controlling the effects of its wastewaters. The wastes that cause the problems include rinse waters from metal electroplating solutions and from acid and alkaline cleaning and pickling solutions. These rinse waters, if discharged into the environment without treatment, can pollute our natural resources, inhibit or destroy natural biological activities, and adversely affect materials of construction. Specific examples of these detrimental effects include the toxicity of heavy metals and cyanides to various forms of aquatic life,[2] the deleterious effect of copper and chromium on biological sewage treatment processes (because of

their toxicity to the microflora),[3] and the corrosive effects of acids and bases on sewer lines and metal and concrete structures.[4,5]

The inactivation or removal of the undesirable constituents from metal finishing wastewaters prior to their disposal is therefore necessary to minimize their detrimental effects on the environment. Several methods exist which accomplish this task with varying degrees of success. The simplest method is the neutralization of an excessively acid or alkaline waste. Inactivation and removal of the metal and cyanide species can be accomplished by oxidation or reduction to a less contaminating state, precipitation to permit removal, or ion exchange for removal or recovery.

Various problems are encountered in the use of any one of these techniques, a few of which include large space requirements, complicated operating procedures, high cost, and insufficient removal of the contaminating species. In addition, the objective of most of the conventional methods of treatment is ultimate disposal or destruction of undesirable constituents, with relatively little attention being given to recovery of the contaminating species or the water.

Reverse osmosis can be used in combination with existing methods of treatment to increase efficiency, or it can be used alone. In combination with existing methods, it can be used to treat water from a continuous destruction process for recycling back to the plant operations, or it can increase the metal ion concentration prior to an ion exchange treatment. If used alone on an individual plating line, it can provide rinse water for recycling and the reclamation of metal salts or other chemicals for reuse.

A discussion of several metal finishing operations, the source of the waste streams and their content, and the reverse osmosis process is given in the progress report covering the first phase of this program.[1]

Review of First Phase

The first phase of the program consisted primarily of determining which membranes, from those commercially available and experimental, were most promising for the reverse osmosis treatment of metal finishing wastewaters. The most important membrane performance criteria were high rejections of specific components, high water fluxes through the membranes, and low decline in flux during operation.

Seventeen different membranes were evaluated for the separation of metal ions, acids, bases, and cyanides from water. They included commercially available asymmetric membranes (approximately 0.002 inch in thickness--500×10^3 angstroms) and ultrathin membranes (1×10^{-6} to 2×10^{-5} inch in thickness--0.25×10^3 to 5×10^3 angstroms). Experimental results using flat sheets of membranes showed that reverse osmosis is feasible and effective in treating these effluents for both pollution control, and metal ion and water recovery for possible recycle. Although no single membrane was found effective for all effluents, membranes for four different polymers showed considerable promise.

Simulated acidic nickel, iron, zinc, and copper plating bath rinses were effectively treated by ultrathin membranes of three polymers: cellulose acetate, cellulose acetate O-propyl sulfonic acid, and β-glucan acetate dimethylaminoethyl ether. Water fluxes were generally above 30 gallons per square foot (of membrane) per day (gfd) at metal ion rejections up to 99.9 percent.

Simulated chromic acid rinses were effectively treated by ultrathin cellulose acetate O-propyl sulfonic acid. This membrane exhibited a water flux (at pH 2.5) of 27 gfd with 95 percent rejection of chromium.

Sulfonated polyphenylene oxide membranes were tested for 95 hours in a highly alkaline (pH 11.4) copper cyanide solution. The rejection was 98 percent for copper and 93 percent for total cyanide, with a water flux of 45 gfd.

Preliminary engineering considerations on the application of reverse osmosis to the treatment and recycle of rinse waters from an acidic copper (sulfate) plating bath were also carried out.

Current Research Program

The objective of this research program may be divided into two parts, (1) the development of those membranes found most promising in Phase I into tubular configurations and (2) the evaluation and development of new second generation membranes for improved metal-finishing waste treatment by reverse osmosis.

- Tubular Ultrathin. Three ultrathin membranes were considered most promising for second phase tubular development because, during the first phase, they were the most effective in treating slightly acidic wastewaters containing copper, nickel, and chromium:

  Cellulose acetate

  Cellulose acetate O-propylsulfonic acid (CAOPSA)

  β-Glucan acetate dimethylaminoethyl ether (β-GADE)

- Second Generation Membranes. The polysaccharide membranes tested in Phase I exhibited poor chemical stability in highly acidic or alkaline wastewaters. Consequently, efforts were directed toward developing and evaluating new, nonpolysaccharide, second generation membranes which would be chemically stable under highly acidic and basic environments. A single polymer membrane that could be used to treat a wide variety of metal finishing waste solutions would provide for greater practicality of the reverse osmosis process for this application.

SECTION IV

EXPERIMENTAL

Polymers

Cellulose Acetate

Cellulose acetate resin was obtained from Eastman Kodak Company. The 398-10 designation indicates 39.8 percent acetyl groups, or approximately 2.5 acetyl groups per molecule (out of a possible three), and a viscosity of 10 seconds. The 360-60 designation indicates 36.0 percent acetyl groups, or approximately 2.0 acetyl groups per molecule, and a viscosity of 60 seconds (molecular weight of 360-60 greater than that of the 398-10).

Cellulose Acetate O-Propylsulfonic Acid

The cellulose acetate O-propyl sulfonic acid (CAOPSA) polymer was synthesized from pure cellulose in the presence of acetic acid.[1] The preparation procedures were designed for the synthesis of cellulose methyl sulfonate O-propyl sulfonic acid (CMSOPSA). However, elemental analysis has indicated the presence of a negligible amount of methyl sulfonate groups and a large amount of acetate groups; thus, CAOPSA is the proper structure. The degree of substitution of O-PSA groups was found to be 0.1 or less.

β-Glucan Acetate Dimethylaminoethyl Ether (β-GADE)

β-GADE was prepared from β-glucan (Pillsbury).[1] The structure was confirmed by elemental analysis. The degree of substitution for dimethylaminoethyl ether was 0.12 and lower.

NS-1 Membranes

The NS-1 membrane is a composite comprised of a microporous polysulfone support film coated with polyethylenimine (PEI) and crosslinked with

tolylene 2,4-diisocyanate (TDI). The thickness of the polysulfone support is approximately 1.8 mils and the quantity of the PEI-TDI on the polysulfone film is equivalent to approximately a 5000-angstrom thick coating. The membrane is fabricated by coating polyethylenimine onto the microporous surface of the polysulfone followed by an interfacial reaction with TDI for the crosslinking step. Heat curing is then necessary to achieve the final rejection and water flux properties.

Membrane Casting

Flat-Cast Membranes

For rapid evaluation of new membrane materials, flat composite membranes were used since they were more easily fabricated than their tubular counterparts. Two new polymers were studied in the flat sheet form: the NS-1 membrane and a copolymer of GANTREZ AN and poly(vinyl alcohol). GANTREZ AN is GAF Corporation's chemical trade name for poly(methylvinyl ether/maleic anhydride).

The GANTREZ AN-poly(vinyl alcohol) condensation copolymer was fabricated in membrane form by immersion of the polysulfone support film into solutions containing varying amounts of the two polymers. The support containing the absorbed polymers was then heat-cured at temperatures varying from 100° to 150°C. The membrane-support composite was cut to size and used in subsequent flat-cell tests.[1]

The preparation of the NS-1 membranes in flat sheets was based on the coating process described above.

Tube-Cast Membranes

The casting procedure for the water-cast tubular ultrathin membrane composites is summarized below.

> The membrane-support composite for a 1/2-inch commercial reverse osmosis tube was cast as follows: the polysulfone support liner was prepared by filling a 0.555-inch-ID

stainless steel tube with a 15-percent solution of Union Carbide P3500 polysulfone in DMF. The tube was drained and a 0.547-inch-diameter aluminum bob was passed through the tube to provide a uniform film of casting solution on the inside wall. The tube was then lowered mechanically in a smooth continuous motion into a one-percent DMF solution, which gelled the polysulfone. After removal from the DMF solution, the tube was filled with a dilute aqueous hydrophilic polymer solution to produce a smooth water drainage, and the membrane casting solution floated on top of this water solution. The tube was drained at a specific rate (draw rate) through a control valve and flow-meter. The wet polysulfone support-membrane composite was then pulled from the stainless stell casting tube and air-dried. The dried composite was attached to a wood dowel and pulled into the commercial fiber glass tube. The ends of the composite were sealed to the tube wall with an elastomeric adhesive.

The NS-1 membrane was fabricated in tubular configurations by immersing a tubular polysulfone support film in an aqueous two-percent PEI solution for ten minutes. Upon removal from the PEI solution, the support liner was immersed in a one-half-percent TDI-hexane solution for thirty seconds. The polysulfone membrane-support composite was air-dried and pulled into a polysulfone-coated 1/2-inch Abcor fiber glass tube. The fiber glass tube, containing the membrane-support composite, was heat-cured at 110°C. Thermolastic adhesive was then applied to the ends of the liner to seal it to the walls of the fiber glass tube.

Reverse Osmosis System

The reverse osmosis test loop contained a 20-liter reservoir, a Model 251-144 Milton Roy Pump, an accumulator (surge-tank), heat exchanger, high-pressure filter, needle valve for system pressure control, and a Rotameter-type flow meter. A detailed schematic diagram and description of the test loop may be found in Reference 1.

Figures 1 and 2 represent the tubular configuration. Figure 1 depicts a cross section of a fiber glass reverse osmosis tube with a polysulfone support liner. Figure 2 is a photograph of the polysulfone liner, Abcor fiber glass tube with end fittings, and the fiber glass tube enclosed in the Tygon product water collection sleeve.

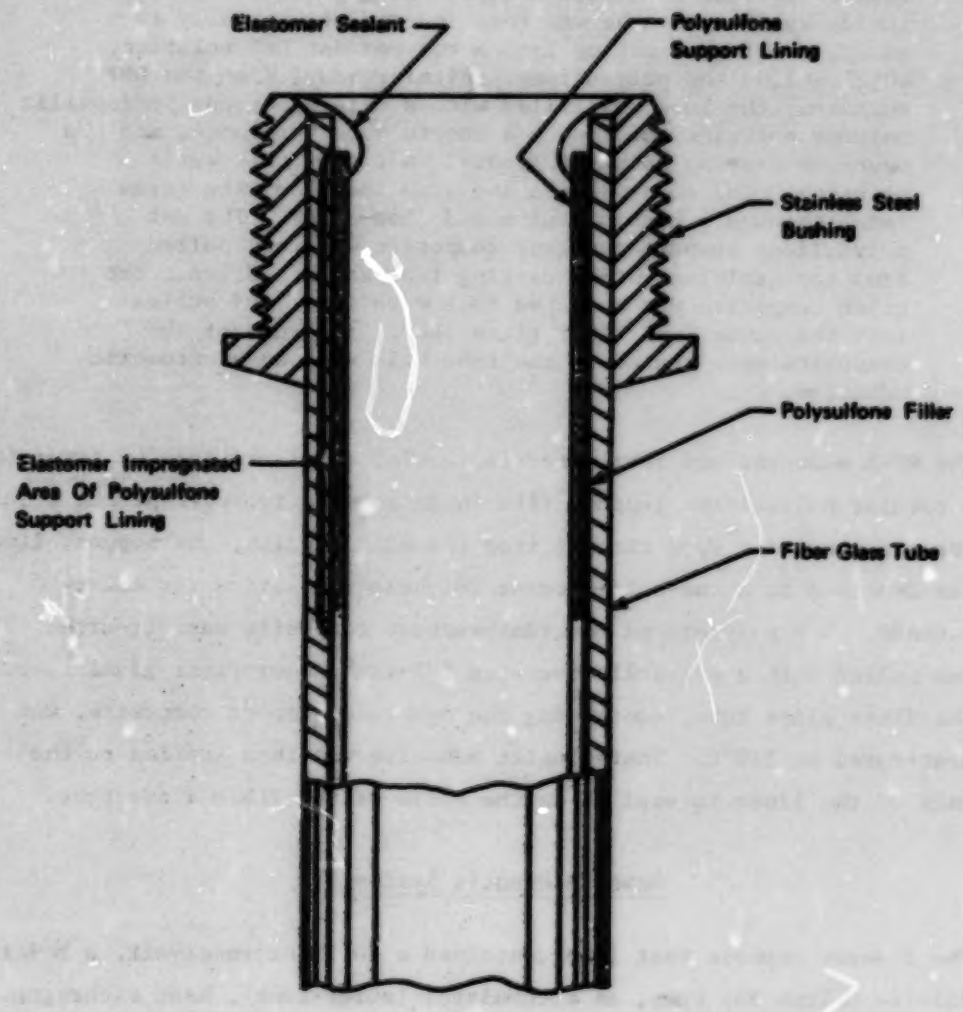

Figure 1. Cross Section of a Fiber Glass Reverse Osmosis Tube with a Polysulfone Support Liner

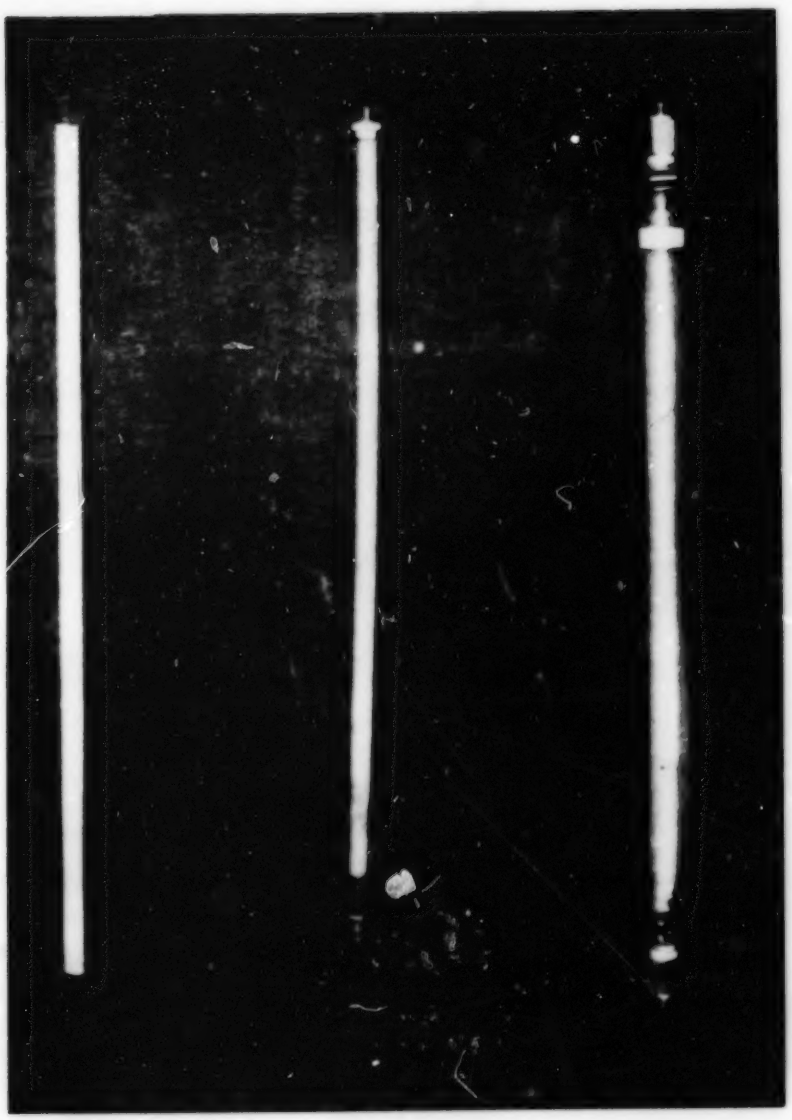

Figure 2. Photograph of Tubular Polysulfone Support Liner (Left), Abcor Fiber Glass Tube with End Fittings (Center), and Fiber Glass Tube Enclosed in a Tygon Sleeve (Right)

A detailed schematic diagram and description of the flat test cell is presented in Reference 1.

Reverse Osmosis Testing

The conditions used to measure the reverse osmosis properties of the tube-cast membrane-support composites and flat reverse osmosis cells were:

Pressure . . . . . 500 psig
Temperature . . . . 25°C (77°F)
Feed Flow . . . . . 1650 to 3350 ml per minute

The metal ion concentration in the feedwater used in the polysaccharide membrane studies was generally about 1000 mg per liter. The simulated rinse waters, used in the nonpolysaccharide membrane studies, were usually 1/10 the concentration of the plating bath solutions. (The formulations for the plating baths used during these studies are presented in Reference 1.)

Water flux measurements were carried out by measuring the rate of flow of the purified water stream from an individual flat cell or tubular reverse osmosis unit.

Rejection measurements were appropriately based either on atomic absorption, total carbon analysis (discussion presented in copper cyanide section) or conductivity determinations of the metal ion content of the feedwater and of the purified water stream. The rejection was calculated as the percent of the total ion content in the feedwater returned by the membrane (see Reference 1).

More detailed feedwater make-up and analyses are given in the appropriate sections of the report.

SECTION V

RESULTS

The results of the experimental program are divided into two separate sections, 1) polysaccharide membranes and 2) nonpolysaccharide membranes. Basically, the polysaccharide section consists of the tubular development of the ultrathin membranes found most promising in Phase I. The nonpolysaccharide section deals with new second generation membranes evaluated during the second half of this program.

Polysaccharide Membranes

In the first phase of the program, only flat-cast membrane-supports were considered. The optimum set of these variables for flat-cast membranes would not necessarily be the same as for tube-cast membranes. Thus, a brief study of these variables was necessary for each polymer to determine its applicability to tubular reverse osmosis. Three polymers were considered: cellulose acetate (two types were used, E 398-10 and E 360-60); CAOPSA and β-GADE. Tube-casting considerations, described in more detail, and reverse osmosis testing using the 1-3/8-inch- and 1/2-inch-ID tubes for casting are given below.

Tube-Casting Considerations

The tube-casting procedures for cellulose acetate E 398-10 had been developed in previous programs for optimum reverse osmosis performance.[6] Thus, the tube-casting development for polysaccharide membranes concerned cellulose acetate E 360-60, CAOPSA, and β-GADE.

Solvent. The solvent used for casting an ultrathin polymer membrane in a tube must meet four basic requirements:

1. It must be a good solvent for the polymer, giving clear, molecular-dispersed solutions.
2. The density of the casting solution should be less than 1.0 so that it does not sink through the aqueous phase.

3. The solvent should have some solubility in water to aid in its removal from the membrane after it is cast. However, too high a solubility in water would lead to gelation of the polymer in the pool of casting solution before it can be formed into a membrane on the support liner. A high solvent vapor pressure also aids in solvent removal from the membrane by evaporation.

4. The solvent must be of a polar nature so that it will spread uniformly on water to give a membrane of uniform thickness.

Cyclohexanone was used as a solvent for all the flat-cast membranes evaluated in the first phase. However, its low water solubility (2.4 percent), high boiling point (157°C), and density of 0.948 eliminated it as a solvent for tube-casting.

Ethyl acetate is an example of an attractive tubular membrane casting solvent because it has a solubility in water of 8.6 percent at 20°C, a density of 0.90, and a boiling point of 77°C. Ethyl acetate was used most extensively in the brief solvent study.

The results of the solvent investigation for each polymer are listed below. In each case many solvent combinations were studied and only the best combinations are given that could be determined within the scheduling of the program.

Cellulose Acetate E 398-10. The best solvent system for cellulose acetate E 398-10 was found to be one part acetic anhydride in 15 parts ethyl acetate. The polymer is first dissolved in acetic anhydride and then diluted with ethyl acetate.

Cellulose Acetate E 360-60. This cellulose acetate has a lower acetate degree of substitution and higher molecular weight than the E 398-10 type; thus its solubilities are different. A clear solution was obtained from the following solvent system: 4 parts acetic anhydride, 1 part cyclohexanone, and 5 parts ethyl acetate.

β-GADE. A ratio of 15 to 1 ethyl acetate to acetic anhydride gave a clear solution for casting.

CAOPSA. It was difficult to find a suitable tube-casting solvent for this polymer. It could be dissolved in acetic anhydride only with prolonged heating. The solvent system consisted of a 1 to 1 ratio of acetic anhydride to ethyl acetate.

Water Additive. Water additives (linear, high molecular weight, water soluble polymers) are necessary to produce a smooth water drainage during tubular casting, which results in uniform membrane thicknesses along the tube. A cationic polyacrylamide (Reten 210, Hercules) was chosen as the standard additive for tube-casting cellulose acetate E 398-10 in earlier programs.[6,7]

Annealing. An annealed membrane will exhibit higher rejections but lower fluxes than non-annealed membranes. Annealing is accomplished by either drying or by exposure to heated water at a specified temperature. Drying the membrane-support composite produces three effects: 1) annealing by dehydration; 2) removal of residual casting solvent; and 3) bonding of the membrane to the support film. The membrane-support composite for the 1/2-inch-ID tube is air-dried and then mounted in a 1/2-inch-ID fiber glass tube. All of the flat cell tests were conducted with membrane-support composites that were not allowed to dry. (This difference between the first-phase flat-cast membrane program and the present tube-cast membrane program caused some differences in reverse osmosis results.)

Reverse Osmosis Testing of Tube (1-3/8-Inch-ID)-Cast Membranes

The objective of this part of the program was to determine tubular casting conditions for the polymers that will produce membranes with good reverse osmosis properties. The polymers were cast on polysulfone supports in 1-3/8-inch-ID tubes, cut from the tubes, and measured in the flat reverse osmosis test cell. This procedure afforded a general screening of tubular casting variables in the shortest possible time and was carried out for cellulose acetate E 398-10 before direct casting in 1/2-inch-ID tubes. The three polymers evaluated in this study were cellulose acetate (E 360-60), CAOPSA, and β-GADE.

Cellulose Acetate (E 360-60). Reverse osmosis performance of ultrathin cellulose acetate (E 360-60) membranes cast into the 1-3/8-inch-ID tube with three casting solution concentrations is given in Table 1. The ions in the feed solution during the test were varied in the following order: sodium chloride, copper, nickel, chromium (pH 5.1), chromium (pH 2.0), and sodium chloride. Each feed solution, except the last, was tested for 24 hours with a total reverse osmosis testing period of somewhat over 120 hours. The last sodium chloride solution was used as a check for membrane degradation and a single immediate reading was compared with the original sodium chloride solution. The test conditions are listed in Table 1.

Table 1 shows that, of the three casting solution concentrations, two-percent cellulose acetate produced a membrane with the highest metal ion rejections. All three membranes exhibited a water flux of 30 gfd after 120 hours of testing. Less flux decline was observed for the thicker membranes cast from the two-percent solution. The magnitude of the membrane thicknesses was generally proportional to the casting solution concentration.

The rejections for copper and nickel were less than those observed during the first phase of this program for flat-cast membranes (99.9 percent).[1] However, the intent of these initial tube-castings was not to optimize, but to show that the membranes could be tube-cast and exhibit good reverse osmosis properties. The cellulose acetate membrane cast from the two-percent solution exhibited higher chromium rejections at both pH's compared to flat-cast membranes. In all cases, the sodium chloride rejections increased from the beginning to the end of the test, indicating no membrane damage.

Typical water flux behavior for the cellulose acetate membrane during the reverse osmosis test, using all the feed solutions, is plotted as a function of time in Figure 3. Changing the feed solution had a negligible effect on the water flux during the 120-hour test. As normally observed in reverse osmosis, the flux declined in the initial

Table 1. Reverse Osmosis Performance of Ultrathin Cellulose Acetate Membranes (E 360-60) in Copper, Nickel, and Chromium Solutions

Conditions:

Tube Cast (1-3/8-inch-ID), 0.14 inch per second draw rate
Flat cell tested
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 1650 ml per minute
Metal feedwater
concentration . . 1000 mg per liter

Concentration of Cellulose Acetate in Casting Solution (percent)	Membrane Thickness <400Å	Water Flux (gfd)		Rejection (percent)				Sodium Chloride Rejection (percent)	
		25 hrs	120 hrs	Cu	Ni	Cr (pH 5.1)	Cr (pH 2.0)	Initial	Final
0.5	Increasing ↓	50	30	71.5	71.5	58.9	23.7	40.0	61.2
1.0		52	30	83.4	83.3	73.2	38.8	57.5	74.2
2.0		44	30	93.6	95.2	89.7	70.1	81.2	86.5

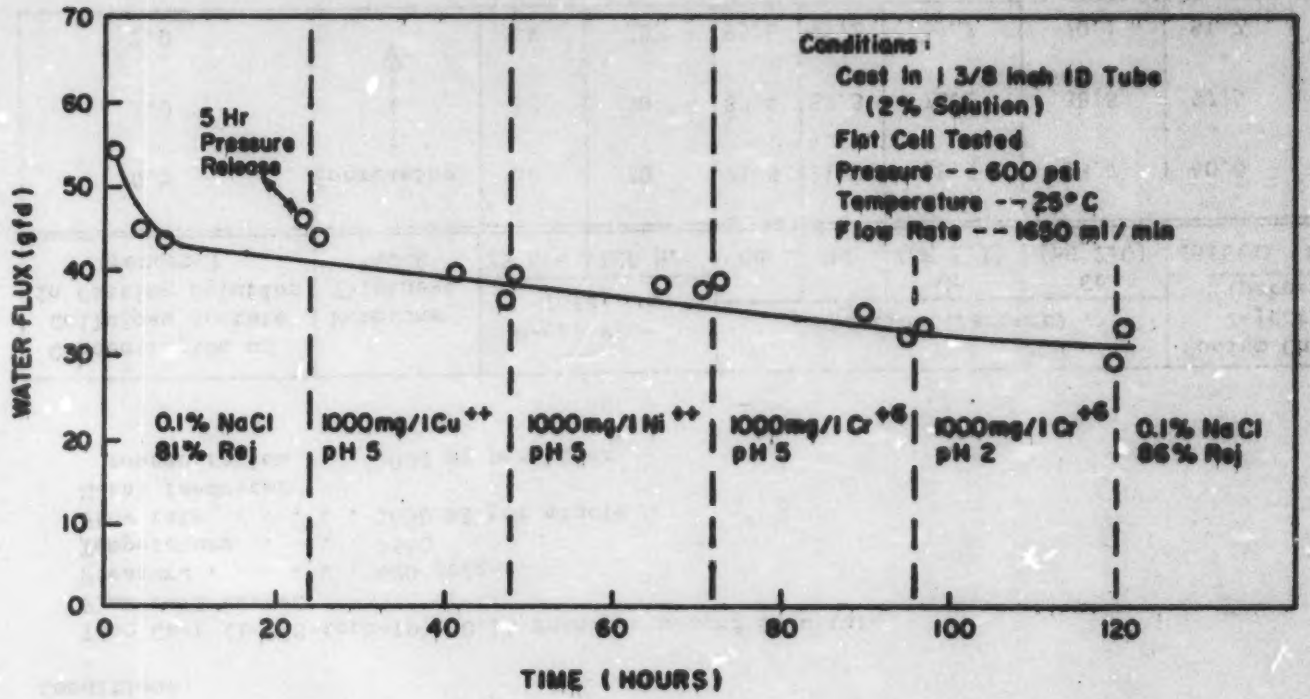

Figure 3, Water Flux Behavior Across Cellulose Acetate (E 360-60) Membrane During Reverse Osmosis Treatment of Metal Ion Solutions

stages of the test. This decline is probably caused by some compaction of the membrane under pressure and by iron oxide fouling in the system. In this case (Figure 3) the flux was leveling-out at above 30 gfd in 120 hours.

CAOPSA. Reverse osmosis tests similar to the cellulose acetate tests described above, but using tube-cast CAOPSA membranes were carried out for 120 hours. However, the rejections were considerably lower than observed for the flat-cast membranes during the first phase of the program. For example, the highest observed rejection for chromium was 71 percent compared to 97 percent for the flat-cast membranes. The water fluxes were all below 10 gfd compared to values of greater than 20 gfd for the flat-cast membranes.

The reason for these poor reverse osmosis properties was the cationic polyacrylamide (Reten 210) solution used for tube casting. CAOPSA exhibits an anionic charge and thus reacts with cationic solutions. This problem was not encountered during the first year because no additives to the water were necessary for flat-casting of these membranes.

Table 2 gives the reverse osmosis performance of two tube-cast CAOPSA membranes using a copper feed solution. One membrane was cast using the cationic polyacrylamide solution, the other using an anionic polyacrylamide solution (Separan AP 30 -- Dow Chemical). This 18-hour test indicates that the anionic material will give tube-cast membranes with rejections and fluxes similar to those observed last year with the flat-cast membranes.

During the first year of this program it was found that the degree of substitution (DS) of the O-propyl sulfonic acid group of CAOPSA was an important factor in obtaining optimum reverse osmosis properties. The higher the DS, the higher the flux and the lower the rejection. Table 3 gives the reverse osmosis performance of several CAOPSA membranes in the DS range of 0.05 to 0.10. The membrane with a DS of 0.05 exhibited the highest copper rejection (97 percent), but exhibited relatively low

Table 2. Effect of Water Phase Additive on Reverse Osmosis Performances of CAOPSA

Conditions:

Tube cast (1-3/8-inch-ID), 1 percent solution, 0.14 inch per second draw rate
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 3350 ml per minute
Feed solution . . . 100 mg per liter Cu^{++}
Length of test . . . 18 hours

Water Phase Additive During Casting	Water Flux (gfd)	Salt Rejection (percent)
Reten 210 (Cationic polyacrylamide)	2.5	85.1
Separan AP 30 (Anionic polyacrylamide)	20.2	95.9

Table 3. Effect of Degree of Substitution (DS) of the O-Propyl Sulfonic Acid Group on the Reverse Osmosis Performance of CAOPSA

Conditions:

Tube cast (1-3/8-inch-ID), 1 percent solution, 0.25 inch per second draw rate
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 3350 ml per minute
Feed solution . . . 1000 mg per liter Cu^{++}
Length of test . . . 24 hours
Water additive . . . Separan AP 30

Membrane No.	DS of OPSA	Thickness (Å)	Water Flux (gfd)	Salt Rejection (percent)
270-48A	Increasing from ∿ 0.05 to ∿ 0.1	300	15.1	96.8
270-49C		650	19.1	90.3
270-49B		—	97.0	49.4
270-49A		800	133.0	35.2

water flux (15 gfd). It is interesting that even though the membrane thickness decreased with decreasing DS, the water flux decreased also. DS is an extremely important factor in regulating the reverse osmosis performance of CAOPSA.

β-GADE. The reverse osmosis performance of β-GADE membranes of varying DS's for the dimethylaminoethyl ether group (DE) is given in Table 4. In this series of tests sodium chloride, copper, nickel, and chromium feed solutions were used; each were run for 24 hours. The tube-casting and measurement conditions are given in Table 4.

Table 4 indicates that the β-GADE with the higher DS (0.12) produced a membrane with high reverse osmosis potential for copper and nickel. The thickness of this membrane was greater than the other two; thus, the flux could be greater, if cast thinner. The flux decline was quite high but leveled off fairly fast. For the β-GADE membranes, a higher flux decline was observed when the chromium feed solutions were used; this is in agreement with results from the flat-cast membranes. The flux decline did not result in membrane degradation because sodium chloride rejection after testing was equal to or greater than that before testing.

The rejections for copper were similar to those for the flat-cast membranes (DS--0.12). For nickel, the rejection was lower than observed earlier. Optimization of casting conditions would be expected to improve the reverse osmosis performance.

The effect of β-GADE membrane thickness on reverse osmosis performance by varying the β-GADE casting solution concentration and draw rate is shown in Table 5. This test series was run for a total of 96 hours using copper, nickel, and chromium feed solutions. Sodium chloride feed solutions were not used before or after, in this case.

The data in Table 5 show that the rejections were significantly higher for the two thicker membranes (270-50C—900Å, 270-50D—600Å). Theoretically, the thickness should not affect the rejection. However, extremely thin membranes are more apt to develop small holes or leaks.

Table 4. Reverse Osmosis Performance of Ultrathin β-GADE Membranes on Copper, Nickel, and Chromium Solutions: Effect of Degree of Substitution (DS) of Diethylaminoethyl Ether (DE) Group

Conditions:

Tube cast (1-3/8-inch-ID), 1% solution, 0.14 inch per second draw rate
Flat cell tested
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 1650 ml per minute
Metal feed water
concentration . . 1000 mg per liter

Membrane Number	DS of DE Group	Membrane Thickness <400A	Water Flux (gfd)		Rejections (percent)				Sodium Chloride Rejection (percent)	
			25 hrs	120 hrs	Cu	Ni	Cr (pH 5.1)	Cr (pH 2.0)	Initial	Final
270-29B	Increasing DS to	Increasing	38	26	98.8	91.4	80.3	44.3	72.0	87.4
270-29A	↓	↓	41	26	95.2	95.4	85.3	66.9	84.8	93.7
270-13A	0.12		68	28	94.1	94.7	68.0	52.2	92.2	92.5

Table 5. Reverse Osmosis Performance of Ultrathin High DS β-GADE (270-13A) Membranes on Copper, Nickel, and Chromium Solutions: Effect of Membrane Thickness

Conditions:

Tube Cast (1-3/8-inch-ID)
Flat cell tested
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 1650 ml per minute
Metal feed water concentration . . 1000 mg per liter

Membrane Number	β-GADE in Casting Solution (percent)	Draw Rate (in./sec)	Membrane Thickness (Å)	Water Flux (gfd)		Rejection (percent)			
				24 hrs	96 hrs	Cu	Ni	Cr (pH 5.1)	Cr (pH 2.0)
270-50C	2	0.15	900	32	22	98.8	99.0	92.9	64.7
270-50D	2	0.50	600	36	26	97.2	98.3	91.2	64.7
270-50E	2	1.50	450	57	40	84.8	83.4	63.4	30.1
270-50F	1	--	<400	57	34	93.4	95.0	84.0	62.7

This was observed particularly in the case of the membrane designated 270-50E (450Å in thickness). The 96-hour water fluxes of the two thicker membranes are not as high as might be desired but, combined with their high copper and nickel rejections, would be adequate for ultimate application.

The thinner membranes (270-50E and 270-50F) were adversely affected by the pH 2.0 chromium solution with lower rejections and considerably higher water fluxes. The lower chromium rejections were also noted for the thicker β-GADE membranes although the fluxes were not affected. Long periods of exposure to pH 2.0 chromium solution would probably degrade most β-GADE membranes—as indicated by increased fluxes and lower rejections.

Conclusions. All three polymers have produced ultrathin membranes cast in 1-3/8-inch-ID tubes that exhibited promising reverse osmosis properties. These polymers were ready for adaptation to the 1/2-inch-ID tubes which will be used in the actual application of reverse osmosis to metal finishing wastes.

Reverse Osmosis Testing of Tube (1/2-Inch-ID) -Cast Membranes

The objective of this task of the program was to carry out short-term reverse osmosis tests in 1/2-inch-ID tubes containing cellulose acetate, CAOPSA, and β-GADE ultrathin membranes to determine casting conditions for high performance reverse osmosis membranes. The solvent systems and general casting conditions were determined from the 1-3/8-inch tube-casting studies. In this task the membranes were cast directly and measured for reverse osmosis performance in the 1/2-inch-ID fiber glass tubes (Abcor, Inc.).

Cellulose Acetate. The cellulose acetate E 360-60 membranes did not show outstanding reverse osmosis properties in the 1/2-inch-ID tubes. Because of a relatively "heavy" solvent system (4:1:5 acetic anhydride: cyclohexanone:ethyl acetate) it was more difficult to cast this polymer

in the narrower diameter tube. This resulted in many leaky and imperfect membranes. Because of these poor results, further development work on this polymer was not pursued.

A sampling of the best reverse osmosis results for the E 360-60 membrane is given in Table 6. The copper ion rejection of 94.5 percent was the highest attainable under the casting conditions developed during the 1-3/8-inch-ID tube-casting studies. This rejection value, coupled with wide variability in the rejections of many membranes cast under the same conditions, indicated that imperfect membranes were being formed. Further casting development would be necessary to cast membranes of cellulose acetate E 360-60 with consistently high reverse osmosis performance.

Another reason for abandoning the 1/2-inch-ID tube-casting development for the E 360-60 membrane was the excellent reverse osmosis performance of 1/2-inch-ID tube-cast cellulose acetate E 398-10 membrane that was observed during concurrent programs in water desalination. The solvent, 15:1 ethyl acetate:acetic anhydride, was ideally suited for 1/2-inch-ID tube-casting. This membrane was considered during the first phase of flat-cell testing, but was not particularly outstanding in reverse osmosis performance. However, during the interval between the end of the first phase of this metal finishing waste program (August 1970) and the second phase, the E 398-10 cellulose acetate membrane was shown to be particularly adaptable to 1/2-inch-ID tubes, giving high fluxes (>20 gfd) and exhibiting excellent sodium chloride rejections (>97 percent) over a period of nine months on a brackish water stream.[8]

The reverse osmosis performance of 1/2-inch-ID fiber glass tubes containing ultrathin cellulose acetate E 398-10 membranes on copper feed solutions is given in Table 7. Several draw rates were used at a previously established casting solution concentration of two percent. The thickness measurement for these 1/2-inch-ID, tube-cast membranes was more difficult and was not carried out in these studies. However, previous studies indicated a thickness variation of approximately 200Å (1.1 inch per second draw rate) to 600Å (0.27 inch per second draw rate).

Table 6. Tubular Reverse Osmosis Performance of Ultrathin Cellulose Acetate Membranes (E 360-40) on Copper Solutions at Two Draw Rates

Conditions:

Cast in 1/2-inch-ID tube (2% solution)
Tested in 1/2-inch-ID tube (2 feet in length)
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 3350 ml per minute
Copper feedwater concentration . . 1000 mg per liter (pH 5)

Membrane Number	Draw Rate (in./sec)	Water Flux (gfd)		Cu Rejection (percent)
		24 hrs	48 hrs	
270-42A	0.24	53	38	94.5
270-43B	0.33	58	42	92.5

Table 7. Tubular Reverse Osmosis Performance of Ultrathin Cellulose Acetate (E 398-10) Membranes on Copper Solutions: Effect of Draw Rate

Conditions:

Cast in 1/2-inch-ID tube (2% solution)
Tested in 1/2-inch-ID tube (2 feet in length)
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 3350 ml per minute
Copper feedwater concentration . . 1000 mg per liter (pH 5)
Length of tests . . 24 hours

Membrane Number	Draw Rate (in./sec)	Water Flux (gfd)	Rejection (percent)
270-42C	0.27	25	99.9
270-43A	0.33	30	99.0
270-48B	0.70	23	99.5
270-48D	1.00	38	98.4
270-50A	1.10	34	96.3
270-50B	1.10	33	98.8

Table 7 shows that the highest copper ion rejections (99+) coupled with adequate fluxes (>20 gfd) were observed for the "thicker" membranes at draw rates below 0.7 inch per second. Because of the observed membrane variability (Table 7, membrane 270-48B should be thinner and exhibit a higher flux than membrane 270-43A) there is an obvious need to optimize the tube-casting process.

Long-term reverse osmosis tests were performed on cellulose acetate E 398-10 ultrathin membranes using several metal feed solutions over 500 hours and using a low pH copper solution (100 mg/l) for 800 hours. During the 500-hour test the membrane exhibited rejections toward copper (97 percent), nickel (95 percent), and chromium at pH 5.5 (96 percent). The flux remained above 40 gfd for these three feed solutions over a period of 240 hours, indicating a very thin membrane. The lower rejections (<99 percent) probably resulted from imperfections.

The second long-term test utilized two copper feed solutions: 1) 100 mg per liter copper ion at pH 2.8; 2) after 500 hours the copper ion concentration was increased to 1000 mg per liter at pH 2.2 and testing carried out for 300 more hours. At the end of 500 hours the flux was above 30 gfd at a copper ion rejection of 96 percent. The change in copper feed solution at 500 hours resulted in a lower flux (28 gfd) and copper rejection (92 percent). The acid rejection during this test was about 90 percent.

Although commercial tubes containing cellulose acetate E 398-10 ultrathin membranes were being optimized for pilot testing at the end of the first six months of Phase II, a membrane of this polymer did not represent a major improvement over commercially available reverse osmosis membranes for the treatment of metal finishing waste. Therefore, further development of this membrane for this application was discontinued.

β-GADE. Ultrathin membranes of β-GADE did not show immediate promise as high-performing 1/2-inch-ID tubular reverse osmosis membranes. All the tubular membranes exhibited very low copper rejections. Typical

results are shown in Table 8. The low rejections for β-GADE were not expected, since it had exhibited considerable promise in earlier 1-3/8-inch-ID tube-casting studies. Because of time considerations on the programs, further attempts to cast β-GADE in 1/2-inch tubes were discontinued.

Cellulose Acetate O-Propylsulfonic Acid. During Phase I the cellulose acetate O-propylsulfonic acid (CAOPSA) membrane, in flat sheets, exhibited the most promising overall reverse osmosis properties. In addition excellent reverse osmosis results were obtained from this membrane when cast in 1-3/8-inch-ID tubes.

At the beginning of the second phase considerable effort was spent trying to fabricate CAOPSA membranes in 1/2-inch-ID two-foot Abcor fiber glass tubes. All tubular-cast membranes exhibited very low salt rejections. Two possible reasons for this poor performance in 1/2-inch tubes were investigated:

1. Poor solubility of the CAOPSA polymer, resulting in premature gelation during the tube-casting process. [As the casting solution is drawn down inside the 1/2-inch-ID tube, solvent diffuses into the water phase and water into the solvent phase. If the polymer gels before the drawing is complete, a potentially leaky membrane results.] Two approaches were taken to alleviate the premature gelation problem: a) varying the polymer synthesis procedure to increase the solubility of the CAOPSA, and b) changes in the solvent system. The original polymer synthesis procedure was altered slightly to increase the solubility of the CAOPSA, by distributing the O-PSA groups more equally throughout the polymer system. This CAOPSA polymer possessed much improved solubility properties and could easily be dissolved in a 7:1 ethyl acetate:acetic anhydride solvent system. The new polymer, however, exhibited approximately the same reverse osmosis properties as unsubstituted cellulose acetate (cellulose triacetate); *i.e.*, adequate salt rejection but water fluxes less than 10 gfd. Concerning the second approach, attempts to alleviate the 1/2-inch tube-casting problem by changing to an acetic anhydride:amyl alcohol solvent system produced results similar to the previous acetic anhydride:ethyl

Table 8. Tubular Reverse Osmosis Performance of Ultrathin β-GADE Membranes on Copper Solutions

Conditions:

Cast in 1/2-inch-ID tubes
Tested in 1/2-inch-ID tubes (2 feet in length)
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 3350 ml per minute
Copper feed
concentration . . 1000 mg per liter (pH 5)
Length of tests . . 24 hours

Polymer	Membrane Number	Draw Rate (in./sec)	Water Flux (gfd)	Rejection (percent)
β-GADE (2% solution)	270-13A-2	0.17	59	22
	270-13A-3	0.31	97	22
	270-13A-1	0.45	100	11
	270-13A-4	0.62	93	30

acetate solvent system (*i.e.*, average salt rejections of 55 percent and fluxes of 40 gfd). This new solvent system should have decreased any water migration into the organic phase and prevented premature gelling of the polymer, since water is considerably less soluble in amyl alcohol than in ethyl acetate.

These findings indicate that the poor membrane performance, observed when CAOPSA is cast in 1/2-inch-ID tubes, is not a result of premature polymer gelling due to water migration in the organic phase, as was previously assumed.

2. Differences in testing procedures between membranes cast in 1-3/8-inch tubes and 1/2-inch tubes. Initially the CAOPSA polymer was cast in the 1-3/8-inch tubes and tested in the flat reverse osmosis test cells with excellent results. However, when CAOPSA was cast in the 1/2-inch fiber glass tubes, the resultant membranes were tested in the tubes. Using this difference in testing procedure as the basic reason for the difference in reverse osmosis performance of CAOPSA membranes cast in 1-3/8-inch-ID and 1/2-inch-ID tubes, the following is a possible explanation:

   > After an ultrathin membrane has been cast in a 1/2-inch-ID tube, the system was then pressurized, the polysulfone support and membrane must conform to the sides of the fiber glass tube. This expansion of membrane and support does not occur in the flat test cells. A certain degree of elasticity must be present in both the support and membrane to allow this expansion process to occur in the tubes without damage to the membranes. If these required elastic properties were not present in the CAOPSA membrane, poor reverse osmosis performance due to rupture in the membrane would result.

   A procedure was designed to eliminate the possible elasticity problem encountered during fabrication of the CAOPSA polymer in 1/2-inch-ID tubes. This was accomplished by pressurizing the polysulfone support liner in the fiber glass tube before casting the ultrathin CAOPSA membrane onto it. Utilizing this technique eliminated the requirement for the membrane to expand to the sides of the fiber glass tube, thus reducing the possibility of membrane rupture during pressurization. The reverse osmosis results obtained in two tubes with ultrathin CAOPSA membranes cast by this procedure are presented in Table 9.

Table 9. Tubular Reverse Osmosis Performance of Ultrathin CAOPSA Membranes

Test Conditions:

Casting 1/2-inch-ID tubes
Tested in 1/2-inch-ID tube (2 feet in length)
Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 3350 ml per minute
Feed composition . . 1 percent NaCl

Tube Number	Reverse Osmosis Results			
	Water Flux Through The Membrane (gfd)		Salt Rejection (percent)	
	0.5 hour	24 hours	0.5 hour	24 hours
50	24	21	91	94
70	29	25	87	90

In Table 9 the sodium chloride rejection was over 90 percent for both tubes after 24 hours. The membrane would be expected to reject divalent ions, such as Cu^{++}, Zn^{++}, or NI^{++}, more efficiently than sodium chloride. The results of this test indicate that CAOPSA may be cast successfully in 1/2-inch tubes by compensating for its lack of elasticity.

Testing of CAOPSA in tubes was terminated at this point because of program time considerations.

Conclusions. Three conclusions may be drawn from the preceeding studies. (1) Cellulose acetate (E 398-10) ultrathin membranes may be successfully cast in 1/2-inch-ID tubes, but it was decided that a membrane of this polymer did not represent a major improvement over commercially available reverse osmosis membranes for the treatment of metal finishing waste.

(2) Ultrathin β-GADE membranes could not be cast successfully in 1/2-inch-ID tubes. The results indicated that considerable development

effort would be necessary to provide an effective tubular β-GADE reverse osmosis membrane. However, this effort was not within the scope of this program.

(3) CAOPSA ultrathin membranes were successfully cast in 1/2-inch-ID tubes by compensating for the inelasticity present in the polymer. Adequate flux and rejection were obtained from these tubes, but further testing was precluded because of program time considerations.

General Conclusion of Tube-Casting Development

In general it was difficult to achieve the very promising reverse osmosis properties for the new ultrathin membranes in the tubular configurations as was observed for the flat-cast membranes during Phase I. However, further tubular casting development would be expected to result in effective membranes. In addition it is important to note that the spiral wrap configuration for reverse osmosis would require flat-casting of the membranes on a water surface followed by continuous lamination to a polysulfone support.[9] A similar process is currently being carried out to produce artificial kidney membranes.[10] Thus, the excellent flat-cast reverse osmosis properties of the ultrathin membranes may be realized more easily in the spiral wrap configuration.

Nonpolysaccharide Membranes

In general polysaccharide membranes were found suitable for the reverse osmosis treatment of metal finishing waste solutions only at pH's from 4 to 8. Many metal finishing effluents, however, are strongly acidic or alkaline (*i.e.*, acid copper pH ∿1; zinc cyanide pH >11). Reverse osmosis membranes comprised of nonpolysaccharide polymers would offer greater chemical resistance to a wide variety of metal finishing waste solutions. The NS-1 membrane originally developed for saline water treatment showed promise for high chemical resistance during a concurrent program funded by the Office of Saline Water. Thus, the NS-1 membrane was applied to metal finishing waste solutions almost exclusively during

the latter half of the program. A small effort was also directed toward new polymers.

NS-1 Membrane

The NS-1 membrane [microporous polysulfone support film coated with polyethylenimine (PEI) and crosslinked with tolylene 2,4-diisocyanate (TEI)] is considered a major new-generation nonpolysaccharide membrane for reverse osmosis. A schematic diagram of the NS-1 fabrication process is given in Figure 4. The final coating on the polysulfone support film consists of 1) amine-crosslinked PEI and 2) TDI crosslinked PEI (urea linkages). An idealized structure of this coating is presented in Figure 5. In this program the NS-1 membrane was evaluated for its reverse osmosis performance on both highly basic (copper and zinc cyanide) and acidic (acid copper chromic acid and Watts nickel) rinses.

Cyanide Rinses. *Reverse Osmosis Tests.* For each test four two-foot reverse osmosis tubes and one flat reverse osmosis test cell, containing NS-1 membranes, were constructed. The simulated rinse water feed solutions consisted of 1/10 the average concentration of common copper- and zinc cyanide plating baths. The copper-cyanide rinse waters contained 1.9 grams per liter cooper and 3.1 grams per liter cyanide at a pH of approximately 11.8. The simulated zinc-cyanide rinse water was prepared by a 1:10 dilution of an actual alkaline zinc plating bath solution obtained from Honeywell Inc. (approximately 1.3 grams per liter zinc and 44.5 grams per liter sodium cyanide at a pH of 12.9).

Samples of the reverse osmosis product water were analyzed for cyanide ions with the Beckman Model 917 Carbon Analyzer and metal ions with a Varian Techtron AA-120 Atomic Absorption Spectrophotometer.

The results obtained from the four tubes and flat test cell during the copper cyanide test are listed in Table 10. The average percent copper and cyanide ion rejections after 500 hours were 99.9 and 98.7 with an average flux of 10.1 gfd. In all cases the flux after 500 hours

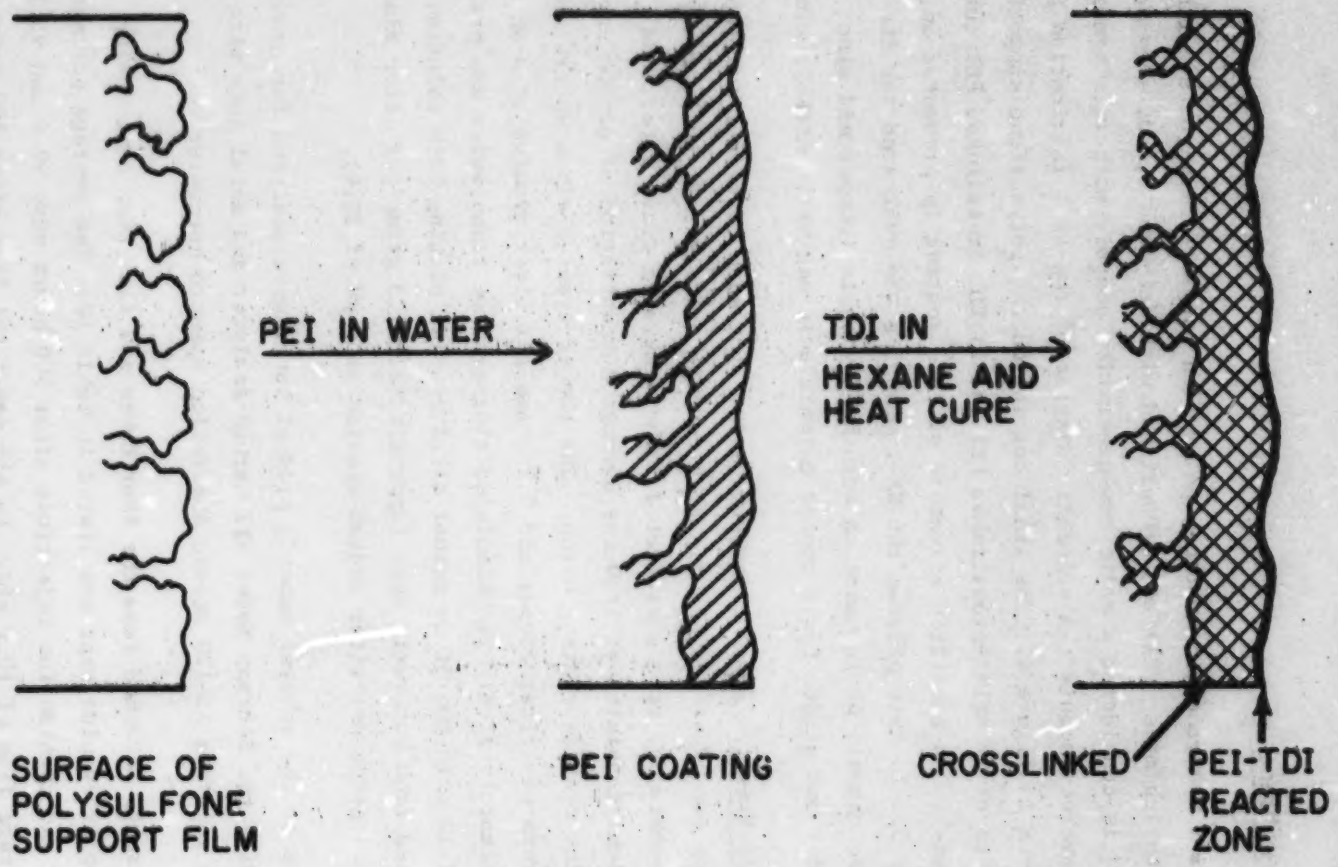

Figure 4. Schematic Representation of NS-1 Membrane

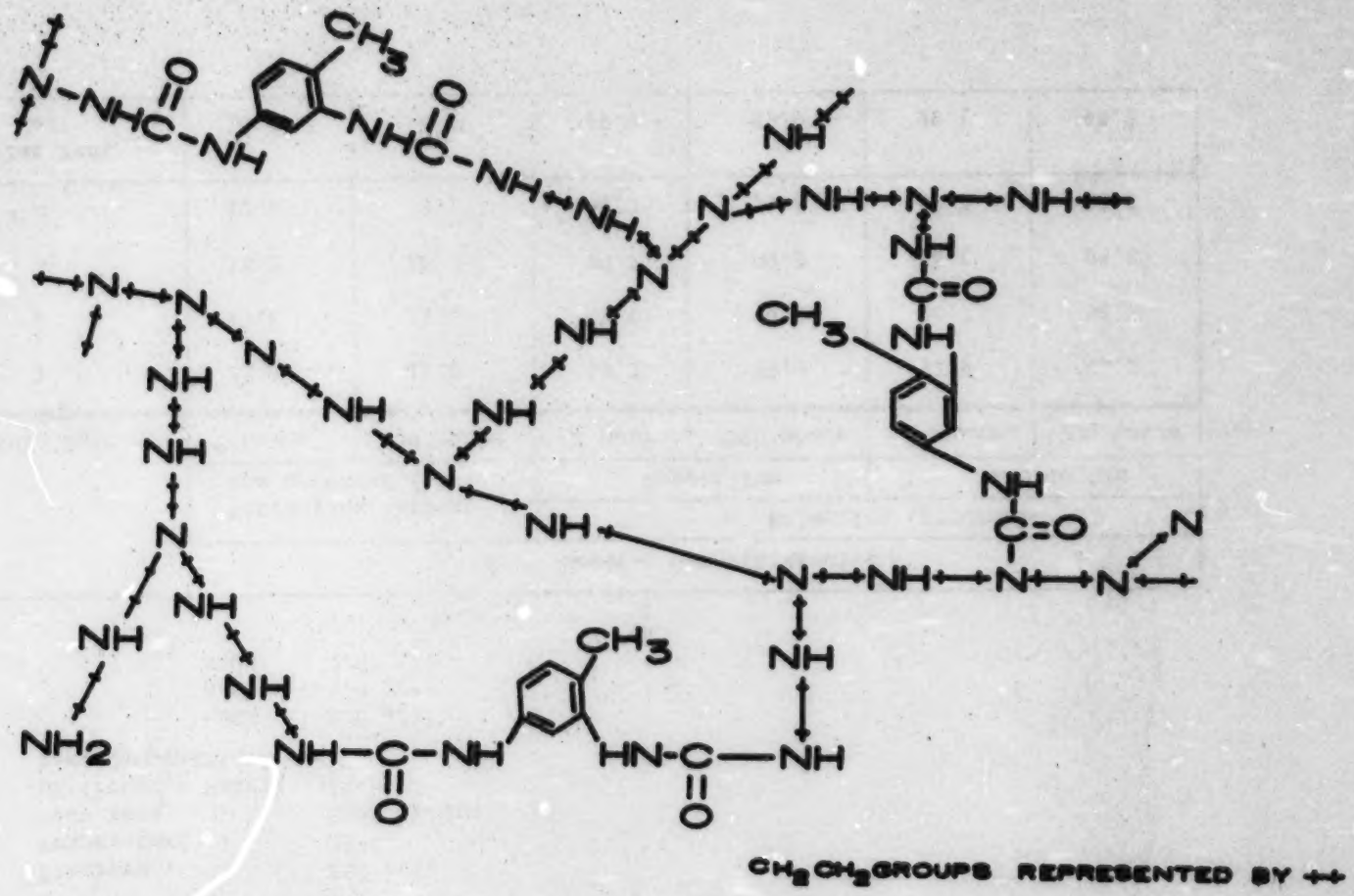

Figure 5. Idealized Structure of Polyethylenimine Crosslinked with m-Tolylene 2,4-Diisocyanate

Table 10. Reverse Osmosis Performance of NS-1 Membrane on Simulated Copper Cyanide Rinse (1/10 of Plating Bath Concentration) Water

Test Conditions:

Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow rate . . . . . 1650 ml/min
pH (Product Water) . 11.8
Feed Composition:

CuCN . . 2.6 g/l
NaCN . . 4.4 g/l
NaOH . . 0.37 g/l

	Reverse Osmosis Results					
	Water Flux Through The Membrane (gfd)		Rejection (percent)			
			Copper Ion		Cyanide Ion	
Tube Number	2 hours	500 hours	2 hours	500 hours	2 hours	500 hours
1	21.1	11.9	99.7	99.9	97.4	98.2
2	17.6	11.6	99.9	99.9	98.7	98.7
3	14.2	10.3	99.7	99.8	98.8	98.8
4	12.2	9.1	99.7	99.8	98.7	98.7
Flat Test Cell	10.8	8.2	99.9	99.9	99.1	99.2

had decreased to approximately 60 to 80 percent of the original values while the rejection remained constant or increased. The tubes with the highest initial fluxes decreased more than those with lower initial fluxes. The flat test cell gave a higher rejection and lower flux than the tubular membranes.

The data presented in Table 10 demonstrate effectiveness of the NS-1 membrane for the reverse osmosis treatment of alkaline copper cyanide rinse waters. The NS-1 membrane was not observed to degrade under the highly alkaline conditions of this test (the ion rejection remained constant or increased). Also, if membrane deterioration had occurred, the water flux through the membrane would have increased with time; the opposite, however, was observed during the test.

Figure 6 is a typical plot of the water flux as a function of time in the copper cyanide system. The flux decreased rapidly with time during the first 100 hours of the reverse osmosis test after which the decline leveled off. This decrease in flux through the membrane may be due to fouling by a colloidal iron oxide which was observed on the surface of the membrane after the 500-hour test.

An indication of how other membranes tested during Phase I compare with NS-1 membranes in copper and cyanide ion rejection is given in Table 11. A direct comparison, however, cannot be made between the rejection data on NS-1 membranes and the other membranes since the tests were performed under different test conditions and time periods. Both ultrathin cellulose acetate O-propylsulfonic acid and asymmetric cellulose acetate degraded under the high pH environments. The sulfonated polyphenylene oxide membrane remained stable for the 95-hour test duration. The NS-1 membrane remained stable for the 500-hour test duration at a higher pH and exhibited significantly higher percent rejections of both copper and cyanide ions than the latter membrane.

An *actual* zinc cyanide plating bath diluted 1:10 (pH 12.9) was utilized during a 340-hour reverse osmosis test of the NS-1 membrane. The data

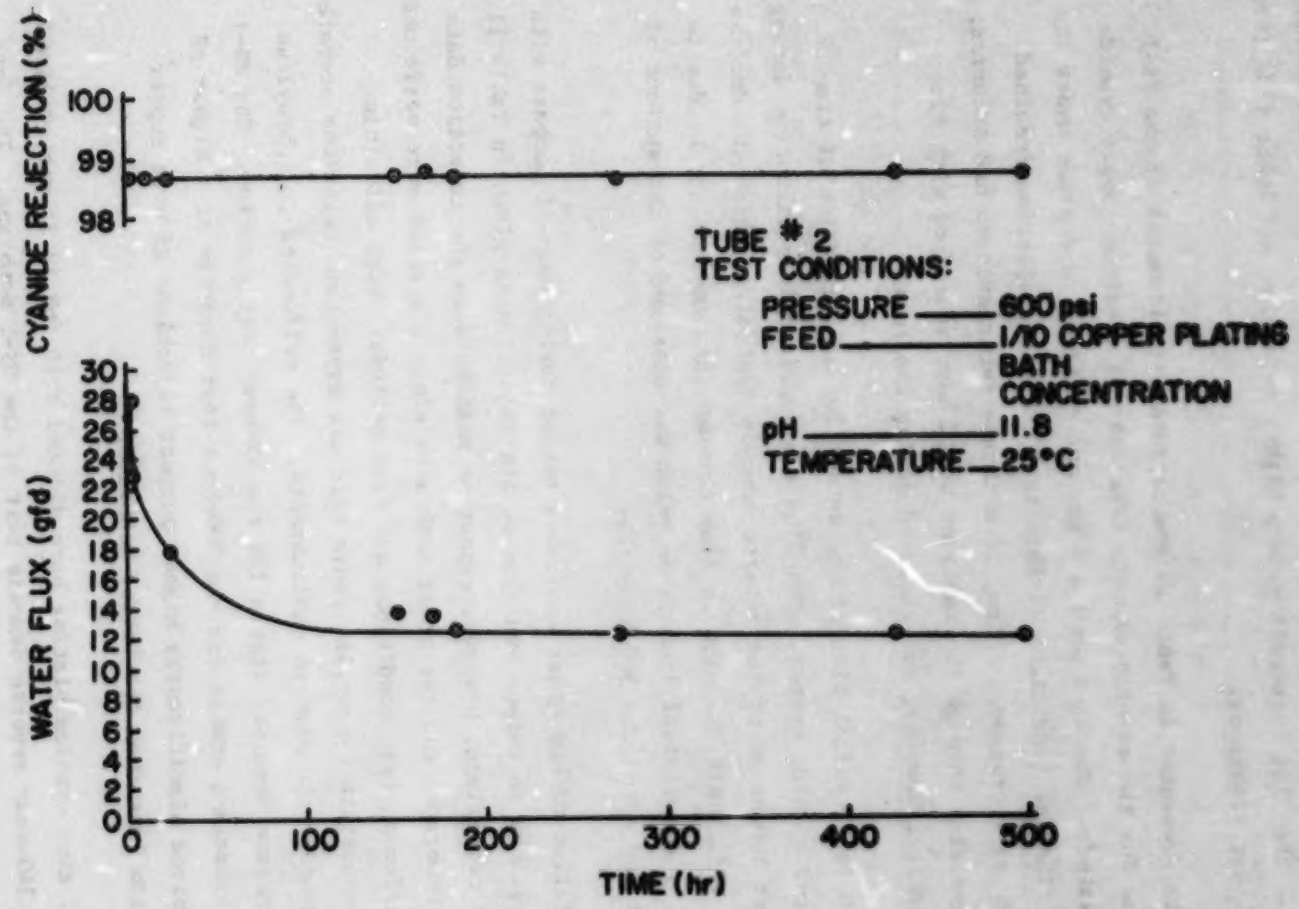

Figure 6. Reverse Osmosis Performance of the NS-1 Membrane with Simulated Copper Cyanide Rinse Water

Table 11. Comparison of Cyanide and Copper Rejections of NS-1 and Other Reverse Osmosis Membranes

Membrane	Cyanide Rejection (percent)	Copper Rejection (percent)	pH	Length of Test (hours)
NS-1	98.7	99.9	11.8	500
Sulfonated polyphenylene oxide*	90.9	95.4	10.4-11.4	95
Ultrathin cellulose acetate O-propylsulfonic acid*	33.3	44.5	10.4-11.4	95
Asymmetric cellulose acetate*	48.1	59.7	10.4-11.4	95

* Rejection data on membranes produced in Phase 1 given in Reference 1.

listed in Table 12 were obtained from three tubes and a flat cell. After the 340-hour test the average rejection of zinc and cyanide ions was 99.8 and 95.5 percent with an average water flux of 11.3 gfd. These results, similar to those obtained during simulated copper cyanide plating bath reverse osmosis tests, indicate that the NS-1 membrane is effective for the treatment of highly alkaline zinc cyanide waste waters.

Figure 7 contains typical plots of water flux and cyanide rejection as a function of time for the zinc cyanide system. These results demonstrate the absence of membrane degradation in the treatment of the highly alkaline (pH 12.9) zinc cyanide plating bath rinse waters by NS-1 membranes.

The significance of this new membrane is illustrated in Table 13 which is a comparison of the reverse osmosis performance of three commercially available membranes with the NS-1 membrane. The first three membranes listed represent commonly used reverse osmosis membranes.

Flux Decline. In both the copper and zinc cyanide tests the water flux at the end of the tests was between 60 to 80 percent of the initial

Table 12. Reverse Osmosis Performance of NS-1 Membrane on Actual Zinc Cyanide Plating Bath Diluted 1:10

Test Conditions:

Pressure . . . . . 600 psig
Temperature . . . . 25°C
Flow Rate . . . . . 1650 ml/min
Feed Composition:

Zn^{++} . . 12.7 g/l
CN- . . 22.4 g/l
NaOH . . 75 g/l
pH . . . 12.9

Tube Number	Reverse Osmosis Results					
	Water Flux Through The Membrane (gfd)		Rejection (percent)			
			Zinc Ion		Cyanide Ion	
	0.5 hour	340 hours	0.5 hour	340 hours	0.5 hour	340 hours
30	16.8	12.9	99.7	99.8	94.5	95.5
33	22.0	14.2	99.6	99.7	94.0	94.5
35	14.8	10.9	99.7	99.8	95.5	96.0
Flat Test Cell	13.7	10.1	99.7	99.8	95.5	96.0

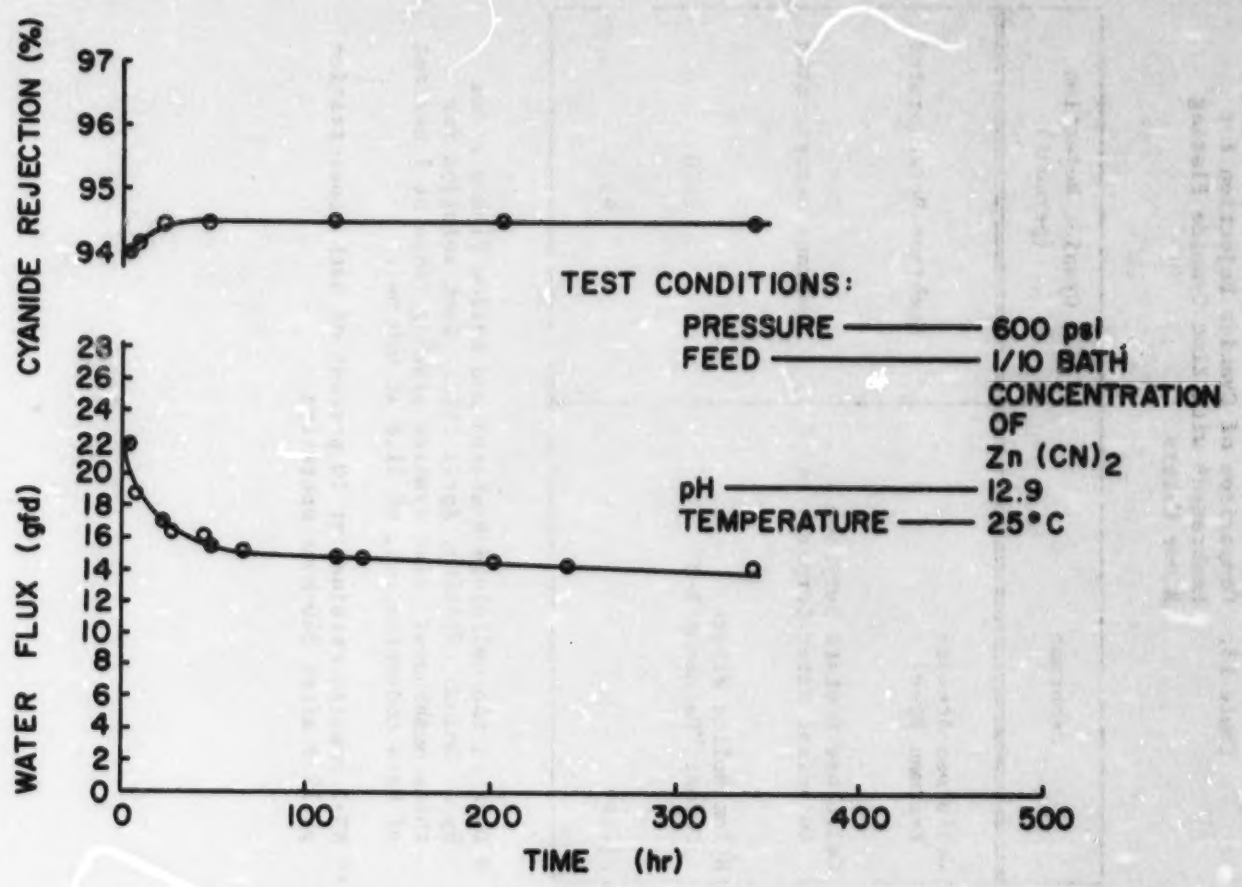

Figure 7. Reverse Osmosis Performance of an NS-1 Membrane with Simulated Zinc Cyanide Rinse Water

Table 13. Comparison of Cyanide Rejection for Membranes* with Zinc Cyanide Plating Rinse Waters

Membrane	Cyanide Rejection (percent)
Cellulose Acetate Eastman RO-97	Membrane Deteriorated
Cellulose Acetate Butyrate Universal Water Corporation	Membrane Deteriorated
Nylon Hollow Fibers DuPont "Permasep B-5"	28.0
NS-1**	95.5

* Data on the cellulose acetates and hollow fibers given by A. Golomb, *Plating*, April 1972. Test solution for these membranes: zinc cyanide plating rinse at 1 percent of bath concentration, pH 11.8 at 600 psi.

** NS-1 results obtained at 10 percent of bath concentration pH 12.9 after 340-hour operation.

readings. This flux decline may be the result of fouling on the membrane surface by colloidal iron oxide which was observed after the 500- and 340-hour tests. Figure 8 is a photograph of the membranes in tubes 1) after casting and no testing and 2) after the testing. This iron oxide apparently is produced by the chemical action of the highly basic cyanide solutions on the stainless steel surfaces of the reverse osmosis system. This problem may possibly be prevented by utilizing plastic materials, such as poly(vinyl chloride), in the system whenever possible. Currently, commercially available plastic tubing and fittings are being utilized in high-pressure reverse osmosis operations. Chemically removing the iron oxide with complexing agents such as citric acid, oxalic acid or ethylenediaminetetracetic acid (EDTA) may also provide a solution to this fouling problem.

Effect of Temperature. The effect of feed temperature on the reverse osmosis performance of the NS-1 membrane was studied by varying the temperature of the zinc cyanide test solution by 10°C intervals between 25° and 55°C. Samples of the water flux across the NS-1 membrane were obtained after the system equilibrated for one hour. The results are plotted in Figure 9 and indicate that flux increased linearly with temperature in this temperature range. The increases in feed temperature from 25° to 55°C caused no significant changes in the cyanide ion rejection in the membrane. Thus if it were not feasible to reduce the rinse water temperature from a hot plating bath prior to reverse osmosis treatment the NS-1 membrane could perform effectively.

Acidic Rinses. The NS-1 membrane was found to be effective for the treatment of highly acidic non-oxidizing metal finishing wastes. Reverse osmosis tests were performed on simulated acid copper, Watts nickel, and chromic acid rinse waters.

Acid Copper. The NS-1 membrane was found to be resistant to chemical degradation under highly acidic conditions (pH 0.5). Ultrathin cellulose acetate membranes did not demonstrate this attractive property. The results of reverse osmosis tests on NS-1 and ultrathin cellulose

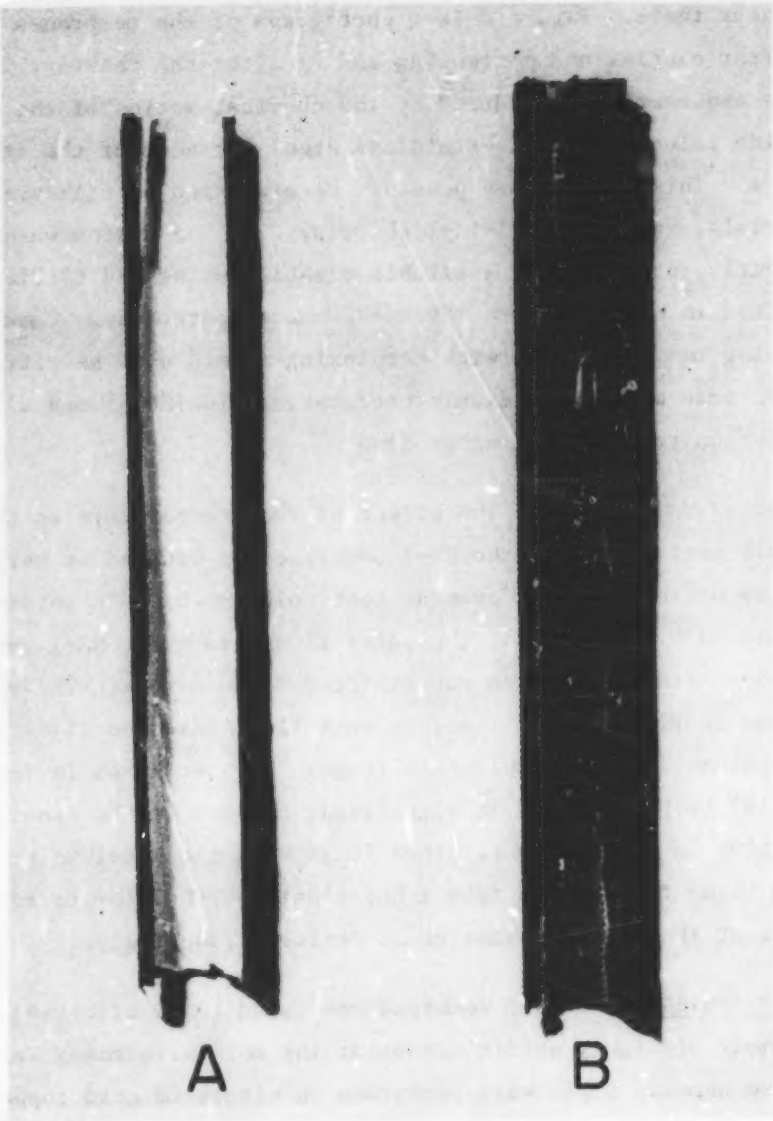

Figure 8. Illustration of Iron Oxide Fouling. Photograph of Cut-away Sections of Reverse Osmosis Tubes (A) After Casting and (B) After 340-Hour Zinc Cyanide Test

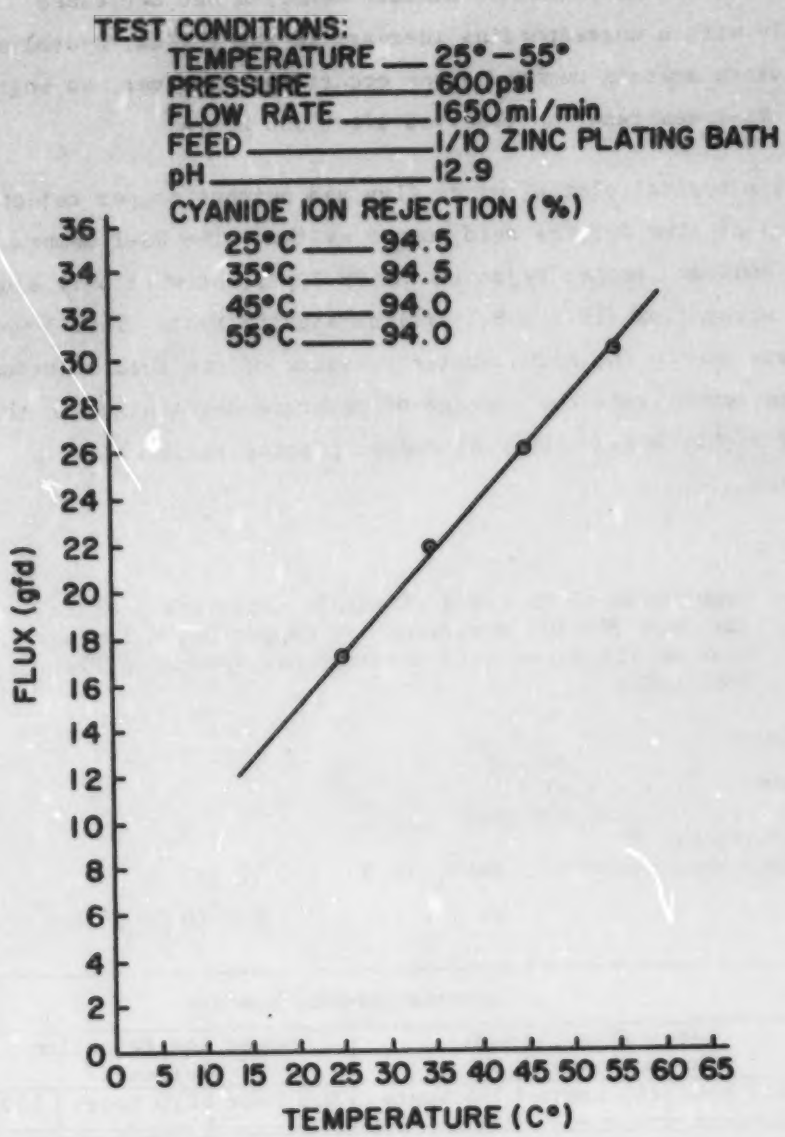
TEST CONDITIONS:
TEMPERATURE ___ 25° – 55°
PRESSURE _____ 600 psi
FLOW RATE _____ 1650 ml/min
FEED _____ 1/10 ZINC PLATING BATH
pH _____ 12.9
CYANIDE ION REJECTION (%)
25°C ___ 94.5
35°C ___ 94.5
45°C ___ 94.0
55°C ___ 94.0
FLUX (gfd)
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36
0 5 10 15 20 25 30 35 40 45 50 55 60 65
TEMPERATURE (C°)

Figure 9. Effect of Operating Temperature on the Water Flux Behavior of NS-1 Reverse Osmosis Membranes

acetate membranes using simulated acid copper plating bath rinse water at pH 0.5 is presented in Table 14. After 210 hours of testing the copper rejection in the cellulose acetate membrane had decreased significantly with a corresponding increase in water flux; hydrolysis of the cellulose acetate membranes was occurring. However, no degradation of the NS-1 membrane was observed after 550 hours.

Figure 10 is a typical plot of water flux and percent copper rejection as a function of time for the acid copper system. The NS-1 membrane exhibited a constant copper rejection at 99.8 percent with only a small decrease in water flux (10.1 - 9.1 gfd) during the test. This lower flux than usual was due to the high osmotic pressure of the feed solution. These results demonstrate the absence of membrane degradation in the treatment of highly acidic (pH 0.5) copper plating rinse waters by NS-1 membranes.

Table 14. Comparison of NS-1 and Ultrathin Cellulose Acetate (Eastman 398-10) Membranes for Copper Rejection and Flux on Simulated Acid Copper Rinse Waters in Flat Test Cells

Test Conditions:

Temperature . . . . . 25°C
Pressure . . . . . 600 psig
Feed Composition:
(1/10 Bath Concentration) $CuSO_4 \cdot 5H_2O$ . . . 20 g/l
pH . . . . . 0.5 (H_2SO_4)

Membrane	Reverse Osmosis Results					
	Water Flux Through The Membrane (gfd)			Copper Ion Rejection (percent)		
	0.5 hour	210 hours	550 hours	0.5 hour	210 hours	550 hours
NS-1	10.1	9.4	9.1	99.8	99.8	99.8
Ultrathin cellulose acetate (E 398-10)	8.8	13.7	—	99.6	85.1	--

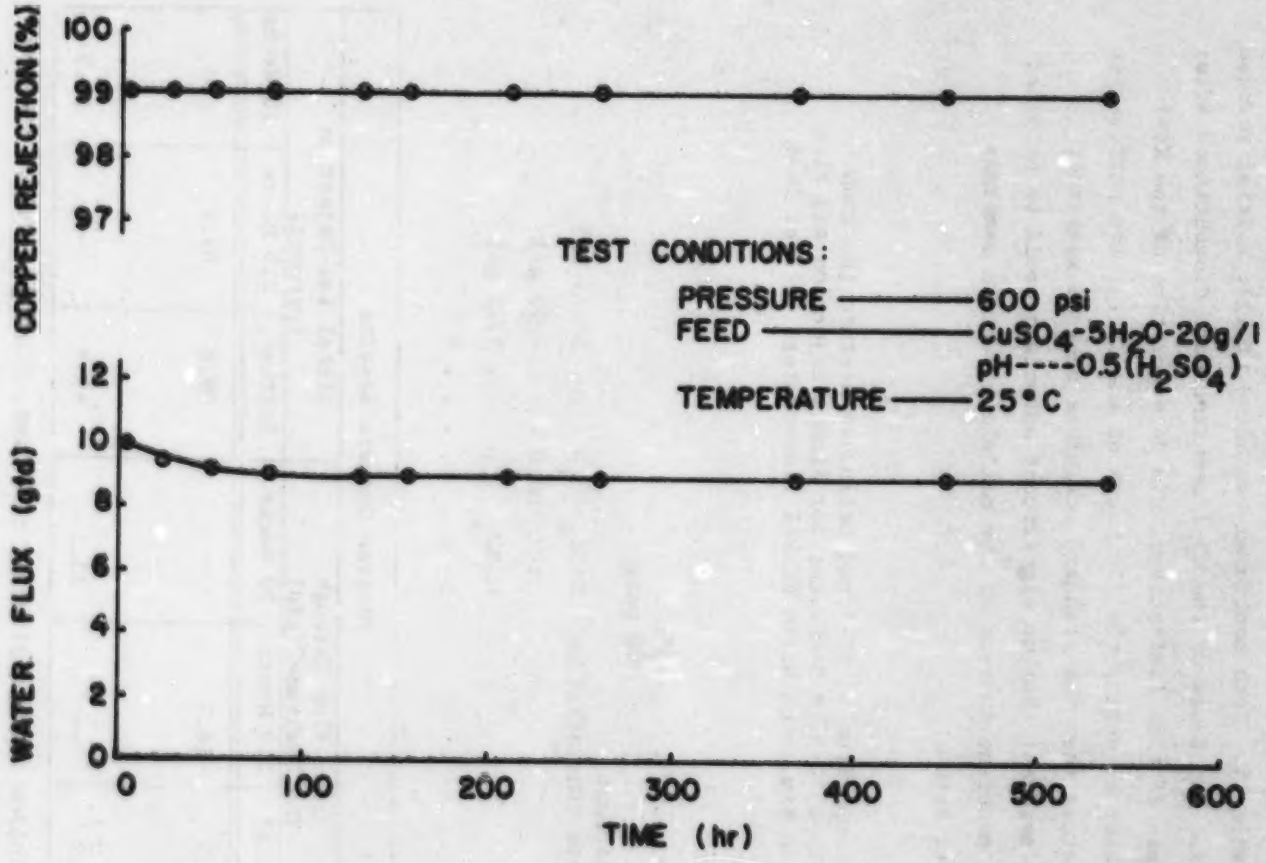

Figure 10. Reverse Osmosis Performance of an NS-1 Membrane with Simulated Acid Copper Rinse Water

Watts Nickel. The results of tests on simulated Watts nickel rinse waters (pH 4.0) and a comparison of the NS-1 membrane reverse osmosis performance with cellulose acetate membranes (Eastman Type RO-97) is presented in Table 15. Both membranes exhibited similar initial reverse osmosis results. The tests on the NS-1 membrane were discontinued after 210 hours because of time limitations. No deterioration of the NS-1 membrane was observed during the 210 hours of the test. Its performance was slightly better than the standard cellulose acetate membrane; however, it is apparent that no significant advantage would be obtained using the NS-1 membrane instead of the cellulose acetate membrane for Watts nickel baths.

Table 15. Comparison of NS-1 and Cellulose Acetate (Eastman Type RO-97)* Membranes for Nickel Rejection and Flux on Simulated Watts Nickel Rinse Waters in Flat Test Cells

Test Conditions:

Temperature . . . . . 25°C
Pressure . . . . . 600 psig
Feed Composition:
(1/10 bath concentration) $NiSO_4 \cdot 6H_2O$ . . . 33.75 g/l
$NiCl_2 \cdot 6H_2O$ . . . 7.50 g/l
H_3BO_3 . . . . . 3.75 g/l
pH 4.0

Membrane	Reverse Osmosis Results					
	Water Flux Through The Membrane (gfd)			Nickel ion Rejection (percent)		
	Initial	210 Hours	10 Weeks	Initial	210 Hours	10 Weeks
NS-1	20.5	16.3	—	99.8	99.9	—
Cellulose acetate (Eastman RO-97)	17.9	—	13.1	99.8	—	98.9

* Data on cellulose acetate given by A. Golumb, *Plating*, October 1970.

Chromic Acid. The NS-1 membrane was ineffective in the reverse osmosis treatment of chromic acid wastewaters at pH 1.5. The feed solution in a 7.5 hour test contained 24.6 g/l chromic acid and 0.247 g/l H_2SO_4 or 1/10 the average plating bath concentration for both materials. Figure 11 illustrates the flux behavior during the test. At the end of 7.5 hours the flux increased by a factor of five. An average chromic acid rejection of 96 percent for the system was observed at the beginning of the test; however, at the conclusion only a 13 percent rejection was recorded. Apparently, the chromic acid oxidizes the PEI-TDI coating at the nitrogen linkages breaking the chains and degrading the polymer. This would cause a decrease in rejection accompanied by an increase in flux. Thus chromic acid wastewaters that have not been adjusted to near neutral pH's could not be effectively treated by NS-1 membranes.

GANTREZ AN-Poly(Vinyl Alcohol) Membranes

A small effort was carried out to determine new membrane polymers that would be resistant to oxidizing acidic metal finishing wastes. The most promising membrane found to date was a material formed by the reaction of GANTREZ AN [poly(methylvinylether/maleic anhydride)] with poly(vinyl alcohol) on a polysulfone support. Water fluxes of over 8 gfd at salt rejections of 90 percent were observed after a 48-hour test at pH 1 for the feed solution.

Table 16 gives the results of the various membranes formed by immersing the polysulfone support in solutions containing varying amounts of GANTREZ AN and poly(vinyl alcohol). The membrane formed by the reaction of 2 percent GANTREZ AN and 0.5 percent PVA solution gave the most promising results.

Conclusions

Five conclusions may be drawn from the data presented in this section:

1. The NS-1 membrane is an excellent candidate for treating alkaline cyanide waste solutions. During the long-term

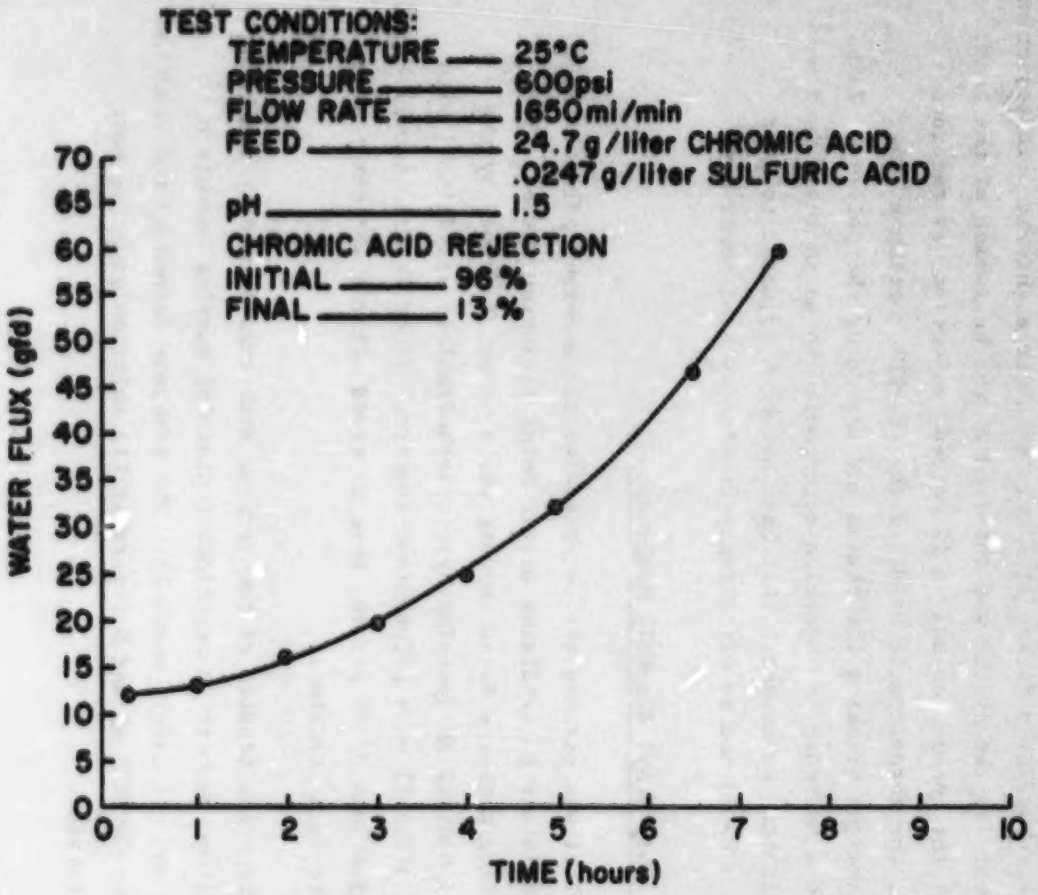

Figure 11. Reverse Osmosis Performance of an NS-1 Membrane with Simulated Chromic Acid Rinse Water

Table 16. Reverse Osmosis Performance of GANTREZ AN-Poly(Vinyl Alcohol) Membranes Prepared from Solutions of Various Polymer Concentrations*

Test Conditions:

Temperature . . . . . 25°C
Pressure . . . . . 600 psig
Feed . . . . . 1 percent NaCl
pH 1.0

Preparation Solution		Reverse Osmosis Performance	
GANTREZ AN (percent in aqueous solution)	Poly(Vinyl Alcohol) (percent in aqueous solution	Rejection (percent)	Flux (gfd)
1.0	1.0	40	1.5
0.5	1.5	32	0.8
1.5	0.5	65	3.2
2.0	0.5	90	8.0

* Membranes were prepared by immersion of a polysulfone support film into aqueous solutions containing the polymers.

tests on alkaline copper and zinc cyanide solutions at pH's of 11.8 and 12.9, respectively, NS-1 exhibited:

a. No membrane degradation during both the 500- and 340-hour tests.

b. An average water flux of 10.1 and 11.8 after 500 and 340 hours of testing. An average water flux decline of 20 to 40 percent for both tests may be attributed to colloidal iron oxide coating on the membrane. The coating apparently is produced by the chemical action of the highly basic cyanide solution on the reverse osmosis system's stainless steel surfaces.

c. High rejection of the solute species (99.9 percent for copper and 98.7 percent for cyanide in alkaline copper plating bath and 99.8 percent for zinc and

95.5 percent for alkaline plating bath at the conclusion of the tests).

d. Stability under high temperatures (no significant changes in cyanide rejection occurred during operation at 55°C while the flux increased approximately 84 percent over the 25°C value).

2. The NS-1 membrane is resistant to highly acidic acid copper rinse waters (pH 0.5) and is probably the only membrane capable of treating these effluents. The membrane exhibited a constant copper ion rejection at 99.8 percent with only a small decrease in water flux (10.1 to 9.1 gfd) during a 550-hour test.

3. The NS-1 membrane is effective for the treatment of Watts nickel rinse waters although not significantly better than commercially available cellulose acetate membranes.

4. The NS-1 membrane is ineffective in the reverse osmosis treatment of chromic acid wastewaters at pH 1.5.

5. A membrane which may have good resistance to chemical degradation in acidic environments has been fabricated from a polymer formed by the reaction of GANTREZ, poly(methylvinylether/maleic anhydride) with poly(vinyl alcohol) on a microporous polysulfone support.

SECTION VI

POSSIBLE APPLICATIONS OF REVERSE OSMOSIS TO THE METAL FINISHING INDUSTRY

During Phase I of this program reverse osmosis was shown to be ideally suited for the treatment of metal finishing effluents. The process can purify plating rinse waters and concentrate the plating ions to levels where recycle to the plating bath is economically attractive. In cases where the concentrated solution cannot be recycled to the plating tank, the concentrate may be refined for the dissolved salts. However, in view of the wide variety of conditions and operations found in the plating industry, reverse osmosis treatment processes must be tailored for each installation and plating process.

Before a reverse osmosis system can be applied to a metal finishing operation, certain parameters must be established:

1. Type and concentration of dissolved material in the rinse water.
2. The degree that various materials are rejected by the membrane.
3. The dragout from plating tanks.
4. Maximum permissible concentration of dissolved material in the last rinse.
5. Evaporation rate from the plating tank.
6. Feed flow rate in reverse osmosis module.

Using these parameters, calculations may be performed to establish the most efficient designs for utilizing reverse osmosis in plating operations. A detailed discussion of typical plating bath lines is presented in Reference 1.

Figure 12 and 13 illustrate design concepts for reverse osmosis systems utilizing NS-1 membranes for the treatment of Watts nickel and zinc cyanide plating wastes. In these closed-loop systems the dissolved material present in the rinse water, due to drag-out, is concentrated by

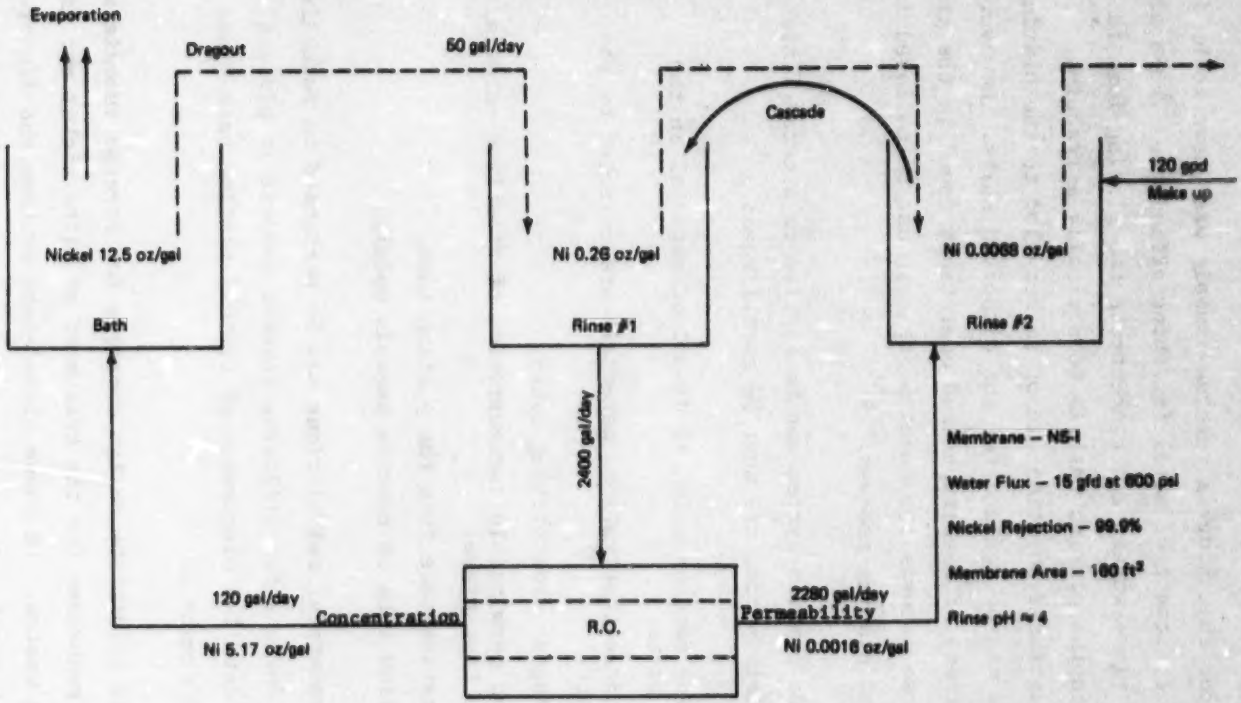

Figure 12. Design Concept for Nickel Plating Waste Treatment Utilizing Reverse Osmosis

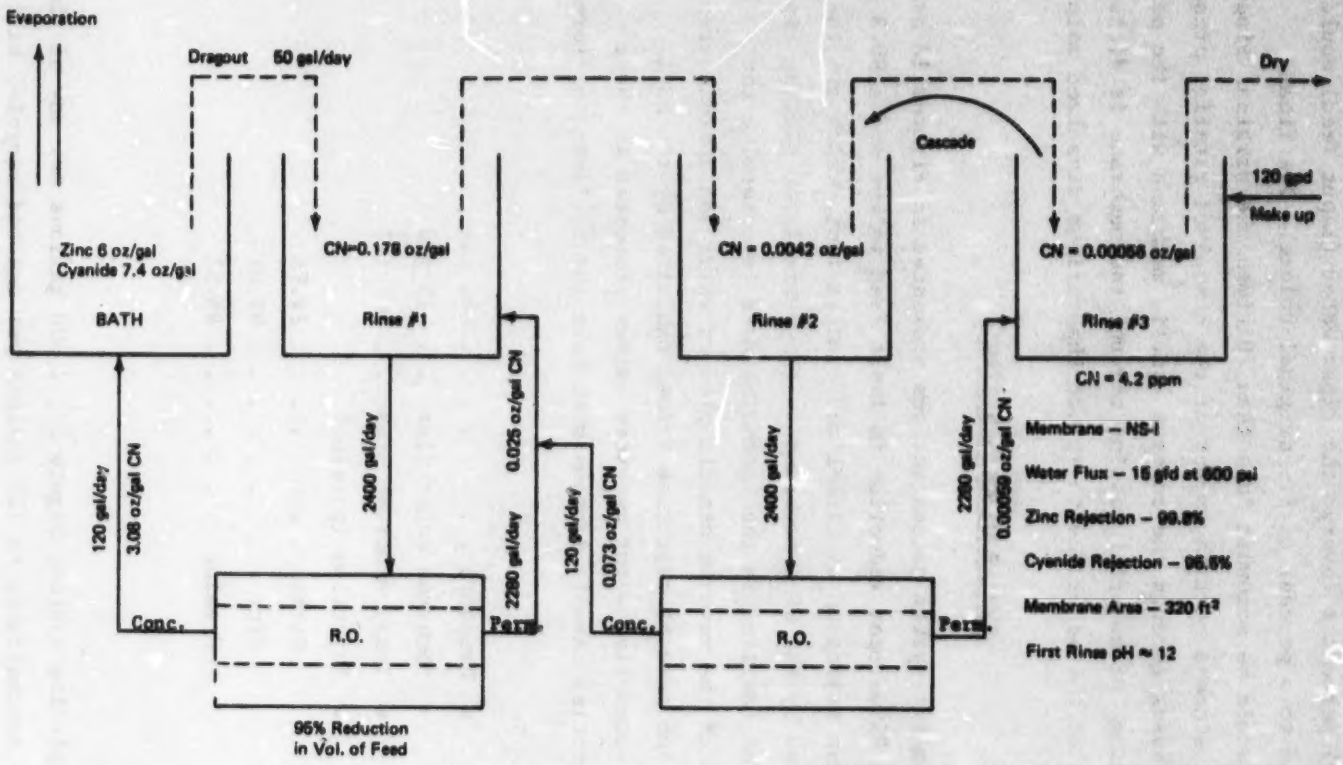

Figure 13, Design Concept for Zinc-Cyanide Plating Waste Treatment Utilizing Reverse Osmosis

reverse osmosis and recycled to the plating rinse. These systems were designed for 95 percent recovery; the rinse water (input feed) would thus be reduced to 5 percent of its original volume. The final concentration would be somewhat less than 20 times the original rinse concentration, since a certain amount of the dissolved material present in the rinse passes through the reverse osmosis membrane with the permeate water. The amount of material passing through the membrane is dictated by the ability of the membranes to reject the various dissolved materials.

Reverse Osmosis System

The reverse osmosis system concentrations presented in Figures 12 and 13 are based on a 95 percent reduction in input feed volume and a 99.8 and 95.5 percent rejection of nickel and cyanide ions, which are the values exhibited by the NS-1 membrane on these simulated plating rinses. The calculations (derived in the Appendix) used to determine the concentrations of the reverse osmosis product water and concentrate required only the percent rejection values exhibited by the NS-1 membrane. To accomplish water recovery values presented in these figures, the reverse osmosis systems must have the following performance parameters:

- Pressure . . . . . 600 psi
- Membrane water flux . . . 15 gfd
- Total membrane area . . 160 ft^2
- Rejection (percent)
  - Nickel 99.9%
  - Zinc 99.8%
  - Cyanide 95.5%

Watts Nickel

In the nickel plating system, Figure 12, 2,400 gallons per day of rinse water would be concentrated to 120 gallons per day and recycled back to the plating bath. The product water (2,280 gallons per day) would be

utilized in the second rinse. With this system only 120 gallons per day of DI water is required for make-up. In Figure 12 it was assumed that the volume lost by evaporation and dragout in the plating bath would be equal to the volume amount of rinse concentrate added to the plating bath. However, this may not be the case in an actual plating operation. In an actual operation, the volume of rinse concentrate added to the plating bath would be dictated by total volume loss in the plating bath due to dragout and evaporation. For example, if this total volume loss was less than the final concentrate volume, the concentrate volume could be further reduced by evaporation.

By utilizing the reverse osmosis system described in Figure 12, 620.4 ounces of nickel per day would be recycled back to the plating bath and 2,280 gallons per day of water is recycled into the rinse system. Assuming that the average cost of nickel is $1.75 per pound, a savings of $67.85 per day for nickel alone could be realized with this operation.

Zinc Cyanide.

The zinc cyanide plating system (Figure 13) must employ a reverse osmosis unit for the first and second rinses, since the cyanide ion is not as efficiently rejected by the membrane as the nickel ion. In this scheme the concentrated rinse water from the first rinse bath is recycled to the plating bath, while the purified water is recycled back to the first rinse. The concentrate from the second rinse is cycled to the first rinse and its purified water is used in the third rinse. This system also requires 120 gallons per day of DI water for make-up. With this reverse osmosis system 369.6 ounces per day of cyanide is recycled back to the plating bath with 2,280 gallons per day of rinse water recycled back through the plating operation. The same plating bath evaporation rate conditions discussed in the Watts nickel bath section would apply in the zinc cyanide system. Assuming that the average cost of zinc is $0.80 per pound, a savings of $30.02 per day for zinc alone could be attained with this operation.

Operating Mode--Reverse Osmosis

The mode of operations used in both Figures 12 and 13 are single-pass operations on the rinse waters using tubular units to support the membrane. To maintain the volumetric flow rate and velocity in the tubes during reverse osmosis treatment, the cross-sectional area or the number of tubes would have to be reduced in downstream sections of the reverse osmosis system.

The minimum amount of space that would be required by the reverse osmosis tubes alone would be 14.7 cubic feet. This volume would contain approximately 235 1/2-inch-ID by 60-inch tubes with a total membrane surface of 160 square feet.

Results

Both the design concepts illustrated in Figures 12 and 13 are represented as closed-loop systems, which would not only result in considerable water and material savings but also eliminate many of the pollution problems associated with plating operations.

The recovery of the materials and water for the two reverse osmosis systems are given below:

	With R. O.	Without R. O.
Make-up deionized rinse water	120gpd	2400gpd
Water recovered for reuse	99 + %	0%
Nickel recovered for reuse	99 + %	0%
Zinc recovered for reuse	99 + %	0%
Cyanide	99 + %	0%

SECTION VII

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SECTION VIII

PUBLICATIONS

Rozelle, L. T., Cadotte, J. E., Nelson, B. R., and Kopp, C. V., "Ultrathin Membranes for Treatment of Waste Effluents by Reverse Osmosis", *Journal of Applied Polymer Science, Applied Polymer Symposia*, in press; also presented at NASA symposium on Polymeric Materials for Unusual Service Conditions, Moffett Field, California, December 1972.

Rozelle, L. T., Cadotte, J. E., Kopp, C. V., and Cobian K. E., *NS-1 Membranes: Potentially Effective New Membranes for Treatment of Washwater in Space Cabins*, ASME Paper No. 73-ENAs-19, New York; also presented at the Intersociety Conference on Environmental Systems, San Diego, July 1973.

SECTION IX

APPENDIX

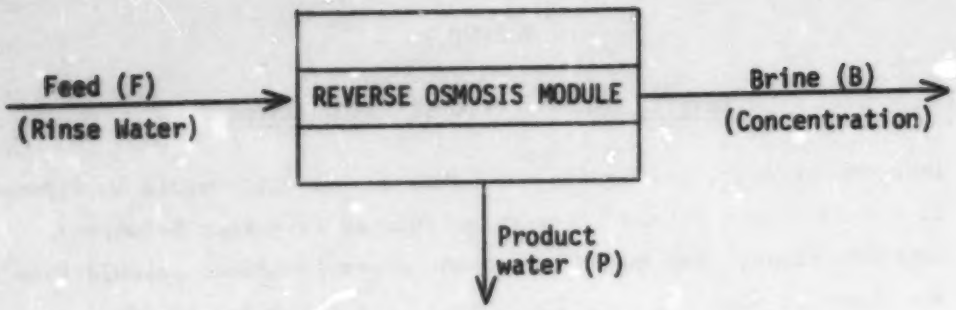
Reverse Osmosis Process Calculations

The concentration values for the brine and product waters in Figures 12 and 13 (pages 56 and 57) were calculated from mass balance determinations. The model and nomenclature for these calculations are shown in Figure 1. In this model, the dissolved solids concentration permeating through any finite area (A) of the membrane was computed by:

$$C_p = (1-R)\beta C_F \qquad (1)$$

This equation expresses the concentration of dissolved solids permeating through the membrane as a function of their concentration in the feedwater (C_F). The fraction of dissolved solids rejected by the membrane (R) and the concentration polarization factor (β) were considered constant in the calculations.

As the feedwater passes through the reverse osmosis module, its dissolved solids concentration (C_F) continuously increases, due to water permeating through the membrane. This change in feed concentration consequently increases the amount of dissolved solids permeating through the membrane with the product water. Therefore, both the permeate and feed concentrations (C_p, C_F) are a function of the feed volume (V_F). A clearer understanding of this process may be obtained by considering reverse osmosis as a continuous method for concentrating unit amounts of the input feed solution. Therefore, an approximation for the function of feed volume (V_F) may be obtained (for materials which are efficiently rejected in the reverse osmosis system) by assuming that the dissolved solids concentration in the feed at a given time (C_F) is inversely proportional to the volume of feed at the same time (V_F):



NOMENCLATURE

C = Concentration of water permeating through reverse osmosis membrane

C_p = Concentration of reverse osmosis module product water

C°_F = Concentration of feed before entering module

C_F = Concentration of feed in reverse osmosis module at a given time

M_p = Total mass of dissolved material in a unit volume of product water

V°_F = Volume of Feed before entering module

V_F = Volume of feed in module at a given time

V_p = Volume of product water ($V^\circ_F - V_F$)

V_{p_f} = Final volume of product water

R = Fraction of dissolved material rejected

β = Concentration polarization--dimensionless

Figure 1. Reverse Osmosis Model and Nomenclature for Mass Balance Calculations

$$\frac{C_F}{C^\circ_F} = \frac{V^\circ_F}{V_F} \qquad (2)$$

where C°_F and V°_F are the initial feed concentration and volume respectively.

A volume balance gives:

$$V^\circ_F = V_F + V_p \qquad (3)$$

where V_p is the volume of the product water.

Combining Equations 2 and 3:

$$\frac{C_F}{C^\circ_F} = \frac{V^\circ_F}{V^\circ - V_p} \qquad (4)$$

$$C_F = \frac{C^\circ_F V^\circ_F}{V^\circ_F - V_p}$$

The feed concentration is slightly over-estimated by this approximation, since a small amount of the dissolved material passes through the membrane with the permeate water.

The total mass of dissolved material transported across the membrane (M_p) can be obtained by integrating C_p from 0 to V_{pf}:

$$M_p = \int_0^{V_{pf}} C_p \, dV_p \qquad (5)$$

Combining Equations 1, 4, and 5:

$$M_p = \int_0^{V_{pf}} (1-R)\beta \frac{C^\circ_F V^\circ_F}{V^\circ - V_p} dV_p$$

$$= (R-1)\beta\, C^\circ_F V^\circ_F \text{ in } \left(1 - \frac{V_{pf}}{V^\circ_F}\right) \quad (6)$$

V_{pf}/V°_F represents the fractional reduction in feed volume exhibited by the reverse osmosis module.

Equation 6 was the expression used in the mass balance computations for the reverse osmosis systems described in Figures 12 and 13. For these computations the concentration polarization factor, β, was assumed to be unity (negligible concentration polarization). Concentration polarization of 1.1 to 1.3 may be found in actual reverse osmosis operations.

Equation 6 offers a relatively easy and accurate method for obtaining the concentration values for both the product water and rinse concentrate, if the values are known for: 1) the fraction of dissolved material rejected by the membranes, and 2) fractional reduction of feed volume exhibited by the reverse osmosis module. By utilizing this equation and standard steady-state mass-balance methods, preliminary design concepts for plating waste treatment with reverse osmosis may easily be evaluated.